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INFLUENCE OF PORE FLUID ON CLAY BEHAVIOR

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ABSTRACT

The understanding of the influence between pore fluids and clay behavior is essential to the design of many components of hazardous and toxic waste containment systems. Without a good understanding of the clay pore fluid interactions, there is no sound basis to project the long-term behavior of these systems.

This study reviews the fundamentals of clay mineralogy and double layer theory as a basis for our understanding of clay behavior in response to changes in pore fluid chemistry. The relationship between soil structure and changes in the physical and engineering properties of clay is then examined. The use of the Gouy-Chapman Model is then proposed to interpret the data of numerous researchers that have studied clay behavior. The study concludes that the application of the Gouy-Chapman Model is generally successful in explaining the influence of pore fluid on clay behavior. The limitations of the model are presented and the needs for further research are discussed.

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INTRODUCTION

The understanding of the interaction between pore fluids and clay behavior requires the interweaving of three normally distinct technical fields. First, the measurement of the soil properties of interest, particularly permeability, requires a working knowledge of geotechnical engineering testing procedures and the influence of details within these testing procedures upon the test result. It requires the knowledge of the testing apparatus, the manifold ways of conducting the tests, the influence of other geotechnical parameters upon the test result, and the natural variability to be expected due to sample preparation and the like. Secondly, a knowledge of the area of clay mineralogy as understood by the geologists and pedologists is required. Thirdly, to understand the interrelationship between the test results and the fundamental clay behavior on a microscopic scale, a knowledge of chemistry is required. This working knowledge of chemistry is essential to the actual understanding of a given test result, which quantitatively measures the effect of a certain pore fluid on a certain clay or a certain clay property. Hence, the study of pore fluid effects on clays requires the interweaving of the technical skills of these three separate disciplines. Further, the understanding of pore fluid effects on clay behavior is essential to the engineering utilization of naturally occurring materials for the containment of hazardous and toxic wastes. Without this knowledge of clay behavior in response to hazardous wastes, any engineering systems design, such as remedial action programs, can have no sound basis on which to project the long-term behavior of that system.

It is the purpose of this paper to examine, at a detailed level, our current understanding of clay behavior in terms of colloidal clay chemistry and clay mineralogy.

Next, hazardous and toxic wastes which are the potential source of pore fluids other than water will be examined from their basic chemistry standpoint. Finally, these separate areas will be merged together through a review of the available published information which presents data relating the effect on certain clay properties due to their exposure to extraneous pore fluids. An attempt will be made to explain the measured behavior in response to the pore fluid stimuli, based on the developed understanding of clay minerology, clay chemistry and pore fluid chemistry.

CLAY MINERALOGY

BASIC CLAY STRUCTURE

The structure of clay minerals is the result of two basic structural units forming a atomic molecular lattice. One unit is an octahedral configuration and the other is a tetrahedral configuration. The tetrahedral configuration is termed a silicon tetrahedron and consists of one centrally located silica atom between four oxygen atoms to form a tetrahedral shape. The silica atom is an equal distance from the four oxygen atoms. Silica tetrahedral groups can be arranged to form a hexagonal network which can be repeated indefinitely to form a tetrahedral sheet. The silicon tetrahedron arranged in a hexagonal network is shown in Figure 1. The oxygen locations can occasionally be filled with hydroxyl ions.

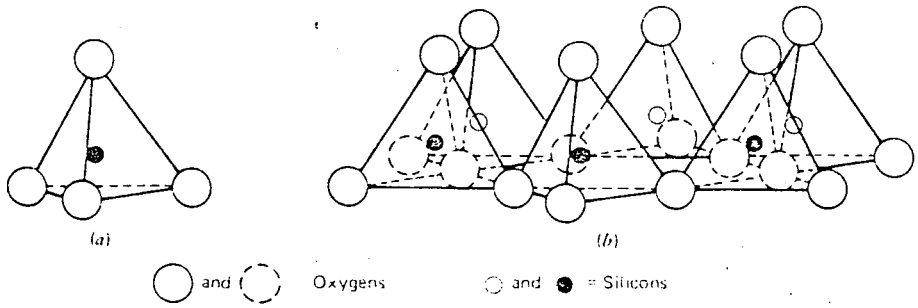


FIGURE 1 - Silica tetrahedron and silica tetrahedra arranged in a hexagonal network.

The second basic building block is an octahedron. The single octahedron unit is formed of central atoms such as aluminum or magnesium surrounded in an octahedral configuration by oxygen atoms. These oxygens in the octahedron may also be hydroxyl ions to balance the central atoms. In like manner to the tetrahedrons, octahedron units can form in a continuous sheet-like structure. Octahedral sheet cations are often mainly aluminum. These sheets are termed gibbsite. When the octahedral sheet cations are predominantly magnesium, these octahedral sheets are termed brucite. The basic octahedral unit and sheet structure of a network of octahedral units is shown as Figure 2.

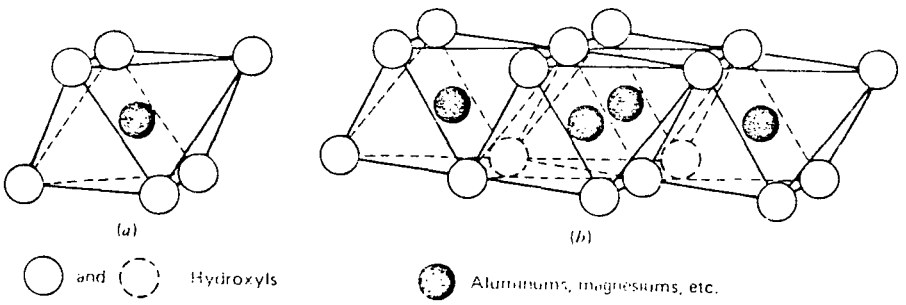


FIGURE 2 - Octahedral unit and octahedral units in sheet structure.

ATOMIC AND MOLECULAR FORCES

The forces holding the atoms and molecules within a clay mineral are generally subdivided into primary and secondary forces or bonds. The primary bonds are considerably stronger relative to the secondary bonds. The energy of primary bonds is in the range of 20 to 200 Kcal per mole as compared to an energy in the range of 1 to 5 Kcal per mole for secondary bonds (Rosenquist, 1968).

Primary Bonds: The three types of primary bonds are ionic, covalent and metallic.

Ionic bonds are the result of the electrostatic attraction between oppositely charged ions. Ions are simply charged atoms resulting from the removal or addition of electrons to an otherwise neutral atom. Positively charged particles are termed cations and negatively charged particles are termed anions. With an ionically bonded molecule, the outer electron shells of the ions are generally complete. The ionic bonds result from the electrostatic attraction of oppositely charged ions. In addition, there can be the electrostatic attraction of oppositely charged ions. In addition, there can be partially covalent ionic bonds and partially ionic covalent bonds.

If the outer electron shell of an atom is incomplete, a sharing of electrons between two or more atoms to complete the shell results in a covalent bond. Pure covalent bonds are common in gases (i.e., O_2, H_2, CH_2), but are not generally found in soils. Typically, a combination of ionic and covalent bonds is found in clay minerals. For example, the bond in silica (SiO_2), the most abundant soil constituent, is about half ionic and half covalent (Mitchell, 1976).

Secondary Bonds: When atomic units are bonded with covalent bonds and sharing electrons which are not symmetrically distributed, the resulting molecule is polar. Polar molecules may be electrically neutral as a whole, but there is a distribution of charge along the molecule. The resulting molecular attraction is termed a dipole force, and dipole bonds can result between polar molecules.

Hydrogen bonds are a specific type of dipole force. If hydrogen is the positive end of a permanent dipole, then the resultant attraction of a negatively charged dipole is

termed a hydrogen bond. Hydrogen bonds are stronger than many dipole forces as they are formed with atoms which have widely different electronegativities. The small size of the hydrogen atom allows the electronegative atom to approach the hydrogen atom more closely. Hydrogen bonds significantly affect the physical-chemical properties of clay minerals as will be subsequently discussed.

Finally, Van der Waals forces result in molecular bonding that is generally weaker than either hydrogen bonds or dipole forces. Although geotechnical engineers generally consider fluctuating dipole bonds as Van der Waals bonds (Bowles, 1979, and Mitchell, 1976), the Van der Waals forces (Van der Waals equation) include all intermolecular forces (Masterton, 1969). Fluctuating dipole bonds, a portion of the Van der Waals bonds, are identified as dispersion or London forces. These dispersion forces, unlike hydrogen or dipole forces, can result from nonpolar or polar molecules. In summary, intermolecular bonds result from what are generally termed Van der Waals forces consisting of dipole, hydrogen and dispersion forces.

STRUCTURE OF CLAY MINERALS

Clay minerals are formed by the stacking of the basic structural unit sheets in a variety of arrangements. The mineral types are generally classified by their unique combination of octahedral and tetrahedral sheets. If the mineral consists of one octahedral sheet and one tetrahedral sheet, it is termed a one-to-one (1:1) mineral. In like manner, clay minerals which consist of a combination of two tetrahedral sheets and one octahedral sheet to form a single layer are known as two-to-one (2:1) minerals. The third major mineral type is known as a two-to-one-to-one (2:1:1) mineral and consists of alternately a tetrahedral sheet, an octahedral sheet, a tetrahedral sheet and an octahedral

sheet. Hence, the three main mineral types a 1:1, 2:1 and 2:1:1 are then subdivided into groups or subgroups depending upon the octahedral sheet configuration.

One-To-One Clay Minerals: The 1:1 minerals are known as kaolinites and actually consist of kaolinite, dickite, nacrite, halloysite (dehydrated) and halloysite (hydrated) minerals (Mitchell, 1976). Discussion will be limited to the kaolinite minerals, the most common of the group. The chemical formula of this mineral which consists of one gibbsite sheet joined with a silica tetrahedron, is $(OH)_8Si_4Al_4O_{10}$. Within the octahedral layer there are generally aluminum atoms, and within the tetrahedral layer the cations are silicon. Because the interlayer bond is primarily ionic (it is primarily a hydrogen bond), the interlayer bonding is substantial. Isomorphous substitution is very low if the crystal lattice energy is high. (Isomorphous substitution is the replacement of a cation in the ideal structure with a cation similar in size and charge density.) Minerological analyses measuring the basal spacing of the kaolinite structure find the basal spacing to be 7.2 Angstroms. The basal spacing is essentially the distance from the base of one layer to the base of the next, or the total thickness of a layer. The cation exchange capacity of the kaolinite clay mineral is generally considered to be 3 to 15 milli-equivalents per 100 grams. A diagrammatic sketch of the structure of a kaolinite sheet is shown on Figure 3.

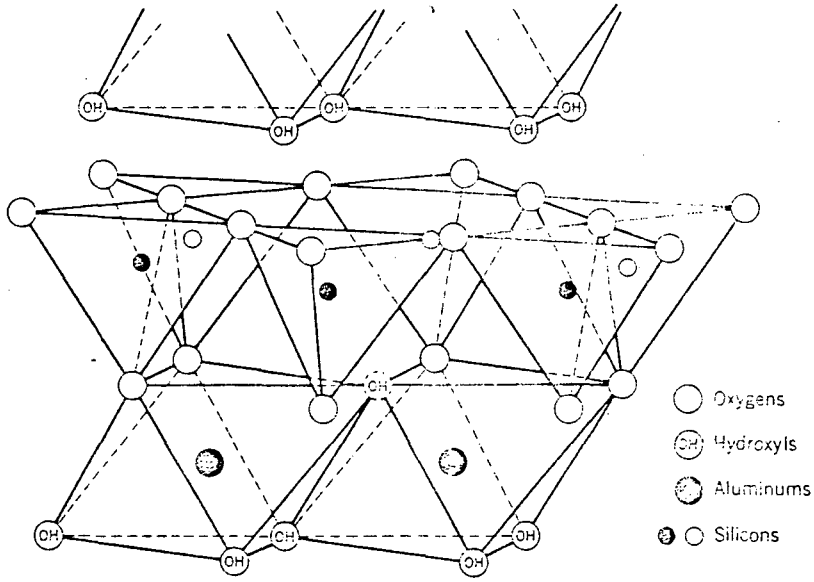


FIGURE 3 - Diagrammatic sketch of the structure of kaolinite (from Grim, 1968).

Two-To-One Clay Minerals: Within the 2:1 family of clay minerals is a group commonly known as smectites. This group of clay minerals was formerly known as montmorillonites, but recent studies have identified montmorillonite as just one of the clay minerals within the smectite group. Smectites also consist of beidellite and nontronite. Montmorillonite by far is the most common of the smectite group, and discussion herein will be limited on that basis. Montmorillonite as a 2:1 mineral consists of two sheets of silica tetrahedron on either side of the gibbsite sheet. Hence, for a montmorillonite that has not experienced any cation substitution or exchange, the chemical formula would be $(OH)_4Si_8Al_4O_{20}(H_2O)n$. In reality, montmorillonite virtually always has some portion of cation exchange with magnesium or sodium. Sodium montmorillonite, a common form of the clay within bentonite, has a chemical formula of $(OH)_4\ Si_8(Al_{3.34}\ Na_{.66})O_{20}nH_2O$. Hence, the octahedral layer cations are generally $Al_{3.34}\ Na_{.66}$ and the tetrahedral layer cations are Si_8 for a given unit. The layers, each consisting of three sheets, are generally stacked with bonding between successive layers by Vanderwaals forces. Due to the charge deficiencies which exist within the lattice, resulting from frequent substitutions, cations may be present between the layers to balance charge deficiencies. These interlayer bonds are therefore relatively weak and easily separated by imposed stresses such as the adsorption of water or other polar liquids. Due to the lattice substitutions within the basic sheets and the cations within the interlayer needed to balance charge deficiencies, the cation exchange capacity is relatively high. It is generally considered that the cation exchange capacity for montmorillonite is between 80 and 150 milli-equivalents per 100 grams. The basal spacing, the distance between layers, can vary from a minimum of 9.6 Angstroms to complete separation or infinity. Presented in Figure 4 is a diagrammatic sketch of the structure of montmorillonite.

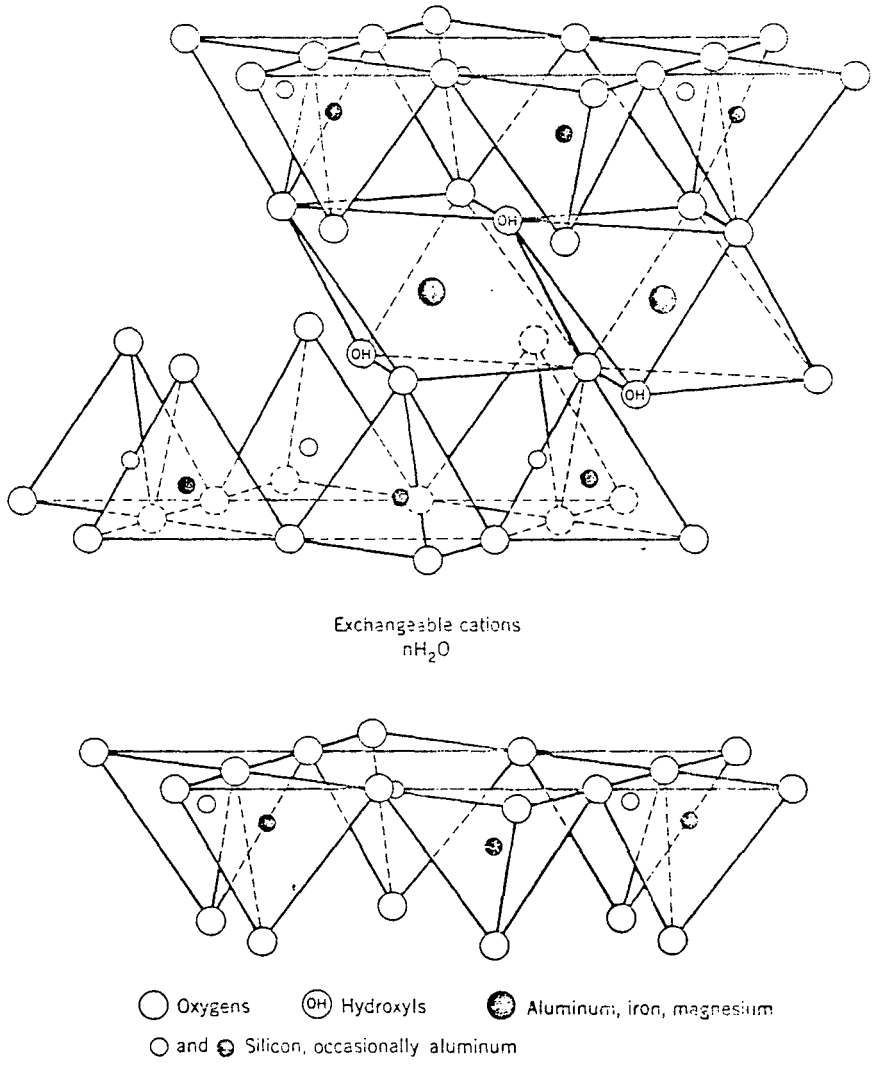


FIGURE 4 - Diagrammatic sketch of the structure of montmorillonite (from Grim, 1968).

Commonly occurring clay minerals encountered in engineering practice are illites. Illites are also known as the micalike clay minerals. Illites, like montmorillonites, are 2:1 minerals (Figure 5). They consist of a gibbsite sheet between two silica tetrahedron sheets, and the layers are bound with a potassium cation populated in the interlayer region. The equation of illite is therefore $(K,H_2O)_2(Si)_8(Al,Mg,Fe)_{4.6}O_{20}(OH)_4$. The octahedral cations are therefore aluminum, magnesium or iron, and the tetrahedral cations can be aluminum or silicon. Within the structure of these clay minerals, the sheets do experience considerable isomorphous substitution. Some of the silicon within the tetrahedral layer are replaced by aluminum ions. This charge imbalance is balanced by the potassium cation populating the interlayer region. The interlayer bonding through the potassium cations is therefore relatively strong. This differs from that of smectites in several ways. The isomorphous substitutions create a charge deficiency of 1.3 to 1.5 in illites and about 0.65 for smectites (Grimm, 1968). The larger charge deficiency in illite is primarily due to the isomorphous substitution in the silicon sheet and therefore is very close to the surface of the unit layer. In smectites, the charge deficiency occurs in the octahedral sheet, which is in the center of the unit layer. Hence, as attraction or repulsion is a function of distance, the charged deficiency nearer the surface results in a stronger attraction for cations. The cation between unit layers in illite is virtually entirely potassium. Because of these two charge deficiency differences, illite structural layers have a relatively fixed position and polar ions do not easily enter between them and cause lattice expansion. This is not the case for montmorillonite. The second major behavioral difference is that the interlayer cations which balance the charged deficiencies are not readily exchangeable. Cation exchange capacity of illite is generally from 10 to 40 as compared to 80 to 150 milli-equivalents per 100 grams for montmorillonite. Figure 5 presents a diagrammatic sketch of the structure of illite.

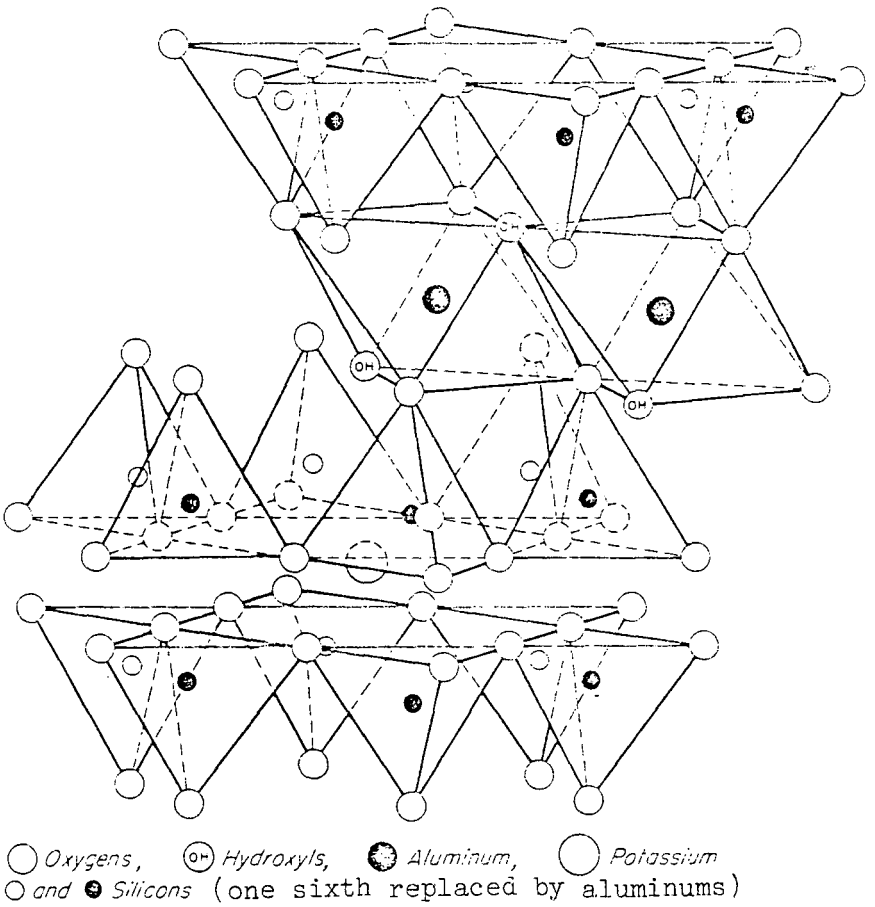


FIGURE 5 - Diagrammatic sketch of the structure of Illite. (after Grim, 1968)

Two-To-One-To-One Clay Minerals: Chlorites have a 2:1:1 structure. They are basically similar to illite except that an organized octrahedron sheet in chlorites replaces the area populated by cations in the case of illite. A diagrammatic sketch of the structural cloride is presented as Figure 6. As shown in Figure 6, the basic layer consists of two tetrahedra sheets bounding a brucite or gibbsite sheet. This is then tied to the next layer with a brucite sheet. The structure is further complicated by the often partial replacement of the central ion in the octahedral sheet with magnesium, aluminum or iron cations. Further, the silica sheets are frequently unbalanced by the substitution of aluminum cations for silica cations within the tetrahedron layer. Thus, the various members of the chlorite group differ in the kinds and amounts of cation substitution and the stacking of successive layers. The basic variety has a chemical formula of $(OH)_4(SiAl)_8(Mg \cdot Fe)_6O_{20}$ (2:1 layer) and $(Mg \cdot Al)_6(OH)_{12}$ (Interlayer). Basal spacing of this mineral, which has four sheets to a layer, is 14 Angstroms. Cation exchange capacity is found to vary from 10 to 40 milli-equivalents per 100 grams. The basic chlorite including its several varieties is quite commonly found.

SCHEMATIC REPRESENTATIONS

Basic building blocks, the silica tetrahedral sheet and octahedral sheet, can be represented schematically. Shown on Figure 7 are the schematics for the silica sheets, the octahedral sheets, and the gibbsite and brucite sheets. Utilizing the symbols for the basic building blocks symbolically, a review of the structure of the primary mineral groups can be made. Figure 8 is a schematic diagram of the structure of kaolinite. This is a 1:1 mineral. Figure 9 shows the basic structure of the smectite groups particularly the montmorillonite, a 2:1 mineral. Shown on Figure 10 is a schematic diagram of the

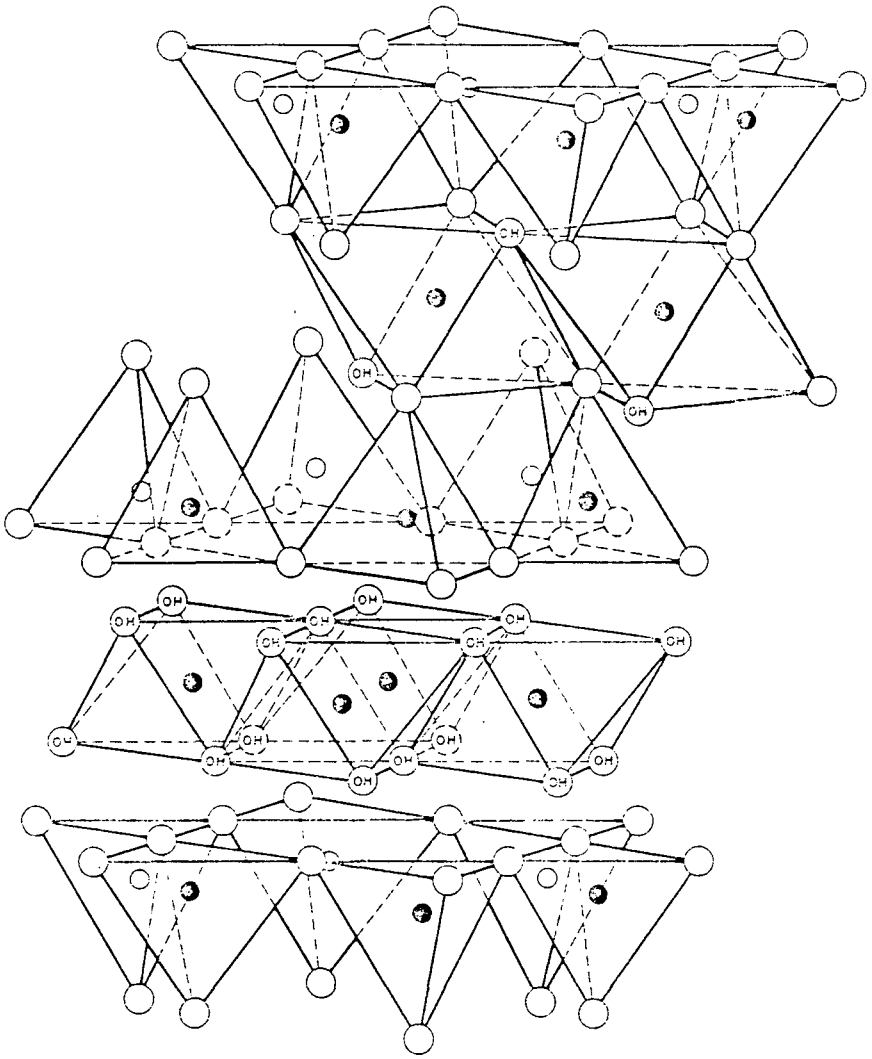


FIGURE 6 - Diagrammatic sketch of the structure of Chlorite. (from Grim, 1968)

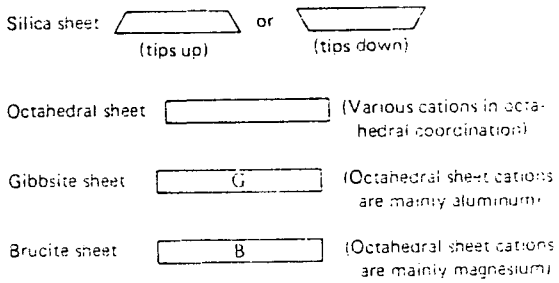


FIGURE 7 - Schematic representations of structural units. (from Mitchell, 1976)

structures of illite and vermiculite, both within the illite family of 2:1 minerals. In Figure 11, a schematic diagram of the structure of chloride is presented.

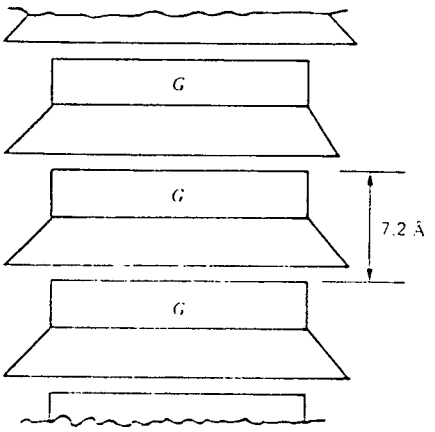


FIGURE 8 - Schematic diagram of the structure of Kaolinite. (from Mitchell, 1976)

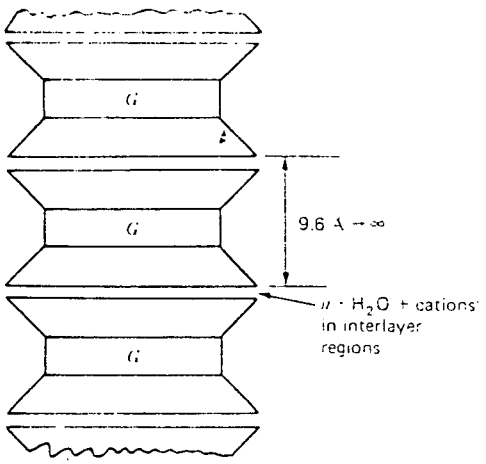


FIGURE 9 - Schematic diagram of the structure of Montmorillonite. (from Mitchell, 1976)

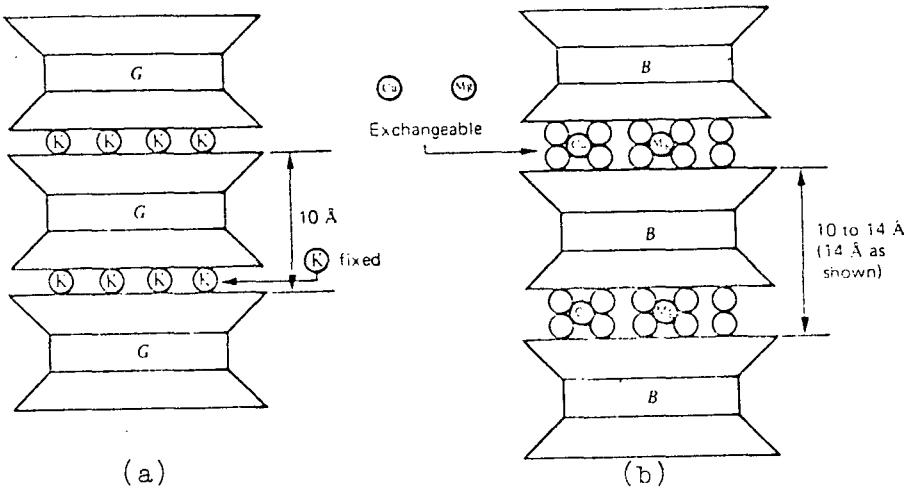


FIGURE 10 - Schematic diagram of the structure of (a) Illite and (b) Vermiculite. (from Mitchell, 1976)

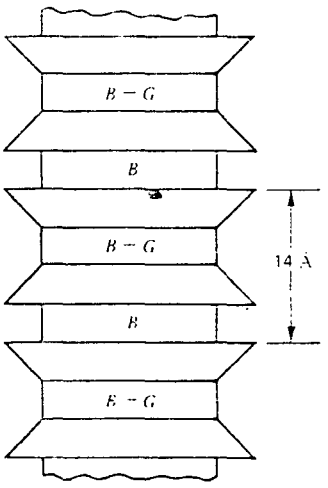


FIGURE 11 - Schematic diagram of the structure of Chlorite. (from Mitchell, 1976)

ISOMORPHOUS SUBSTITUTION

Isomorphous substitution is frequently used in the characterization of the clay mineral structure. Isomorphous substitution is simply the replacement or substitution of cations within the basic structure. Isomorphous substitution or replacement of one cation for another frequently results in charge deficiencies. That is, if, for example, one cation of a +3 charge is substituted with a cation of a +2 charge, the charged efficiency of +1 exists in the area of that substitution. The cation exchange capacity of a clay mineral is a quantified measure of that clay mineral's capacity for cation substitution. An ion, a positive or negative charged particle, results from the removal or addition of electrons to a neutral atom. If electrons are removed, that particle becomes positively charged, or a cation. As cations exist within the mineralogical structure of clays, the cation exchange capacity is a measurement of the propensity of cations within this clay mineral to be replaced or substituted.

The determination of cation exchange capacity is at present somewhat arbitrary as numerous methods have been proposed for this determination. Grimm, 1968, recommends that the measurement be made by saturating the clay NH_4+ and then determining the amount held at a pH of 7. Grimm goes on to say that a determination of the exchangeable cation composition is also very difficult. It involves the complete replacement of all exchangeable cations by another cation which is not already present in the clay mineral structure. After the complete replacement, an accurate analysis of cations present in the solution must be made. Finally, an assessment of the cations that go into the solution from any soluble substances must also be made. He suggests the use of the flame filter meter for the analysis of the ion in the replacing solution.

The replacement of cations within the mineral structure, and thus the cation exchange capacity, can result from (1) broken bonds within the clay mineral structure; (2) substitutions within the lattice structure; and/or (3) replacement of the hydrogens which are part of the exposed hydroxides (an intregal part of the structure). It is the second cause of cation excnange capacity, substitution within the lattice structure, that is the major contributor to the total cation exchange capacity.

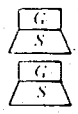
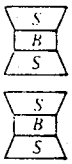
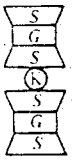
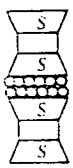
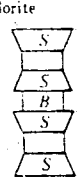
There are many factors which influence the cation exchange capacity. These include crystalline particle size, the temperature environment of the exchange reaction, and the concentration and nature of the ion used in the replacement substitution. Despite these many factors, the cation exchange capacity of various clay minerals generally falls within certain limits. This cation exchange capacity is useful in the identification of clay minerals. Various groupings and classifications can be utilized to provide a common basis for the combinations of clay mineral structure. For the purposes of this paper, the grouping has generally followed those presented by Mitchell, 1976. Presented in Table 1 is a summary of clay mineral characteristics, which will subsequently be useful when examining the behavior of various clay minerals in response to various pore fluids.

To summarize this section of the report, it is noted that the understanding of the clay mineral structure is essential for our understanding of the macroscopic and microscopic behavior of clays in response to various pore fluids. The summary presented herein is based upon the commonly accepted models of clay structure. The information presented in the previous sections is considered general knowledge and is contained in numerous texts, but the writer relied heavily upon three major references in the preparation of this section. These references were Mitchell, 1976; Grimm, 1968; and Van

Olphen, 1977. The reader is referred to these texts if more detailed information is desired.

TABLE 1 - SUMMARY OF CLAY MINERAL CHARACTERISTICS

Structural
1. Silica Tetrahedron: Si atom at center. Tetrahedron units form hexagonal network = $Si_4O_6(OH)_4$
2. Gibbsite Sheet: Aluminum in octahedral coordination. Two-thirds of possible positions filled. $Al_2(OH)_6$—O-O = 2.60 Å.
3. Brucite Sheet: Magnesium in octahedral coordination. All possible positions filled. $Mg_3(OH)_6$—O-O = 2.60 Å

Type	Sub-Group and Schematic Structure	Mineral	Complete Formula/Unit Cell[a]	Octahedral Layer Cations	Tetrahedral Layer Cations	Structure: Isomorphous Substitution	Structure: Interlayer Bond
	Allophane	Allophanes	Amorphous	—	—		
1:1	Kaolinite 	Kaolinite	$(OH)_8Si_4Al_4O_{10}$	Al_4	Si_4	Little	O-OH Hydrogen Strong
		Dickite	$(OH)_8Si_4Al_4O_{10}$	Al_4	Si_4	Little	O-OH Hydrogen Strong
		Nacrite	$(OH)_8Si_4Al_4O_{10}$	Al_4	Si_4	Little	O-OH Hydrogen Strong
		Halloysite (dehydrated)	$(OH)_8Si_4Al_4O_{10}$	Al_4	Si_4	Little	O-OH Hydrogen Strong
		Halloysite (hydrated)	$(OH)_8Si_4Al_4O_{10}.4H_2O$	Al_4	Si_4	Little	O-OH Hydrogen Strong
	Montmorillonite $(OH)_4Si_8Al_4O_{20}.NH_2O$ (Theoretical Unsubstituted)	Montmorillonite	$(OH)_4Si_8(Al_{3.34}Mg_{.66})O_{20}.nH_2O$ ↓ $Na_{.66}$	$Al_{3.34}Mg_{.66}$	Si_8	Mg for Al. Net charge always = 0.66- /unit cell	O-O Very weak expanding lattice
		Beidellite	$(OH)_4(Si_{7.34}Al_{.66})(Al_4)O_{20}.nH_2O$ ↓ $Na_{.66}$	Al_4	$Si_{7.34}Al_{.66}$	Al for Si. Net charge always = 0.66- /for unit cell	O-O Very weak expanding lattice
		Nontronite	$(OH)_4(Si_{7.34}Al_{.66})Fe_4^{3+}O_{20}.nH_2O$ ↓ $Na_{.66}$	Fe_4	$Si_{7.34}Al_{.66}$	Fe for Al. Al for Si. Net charge always = 0.66- /for unit cell	O-O Very weak expanding lattice
2:1	Saponite 	Hectorite	$(OH)_4Si_8(Mg_{5.34}Li_{.66})O_{20}.nH_2O$ ↓ $Na_{.66}$	$Mg_{5.34}Li_{.66}$	Si_8	Mg, Li for Al. Net charge always = 0.66- unit cell	O-O Very weak expanding lattice
		Saponite	$(OH)_4(Si_{7.34}Al_{.66})Mg_6O_{20}.nH_2O$ ↓ $Na_{.66}$	Mg, Fe^{2+}	$Si_{7.34}Al_{.66}$	Mg for Al. Al for Si. Net charge always = 0.66- /for unit cell	O-O Very weak expanding lattice
		Sauconite	$(Si_{6.54}Al_{1.06})Al_{4.44}Fe_{.34}Mg_{.36}Zn_{4.80}O_{20}(OH)_4$ ↓ $Na_{.66}$ $.nH_2O$	$Al_{.44}Fe_{.34}Mg_{.36}Zn_{4.80}$	$Si_{6.54}Al_{1.06}$	Zn for Al	O-O Very weak expanding lattice
	Hydrous Mica (Illite) 	Illites	$(K,H_2O)_2(Si)_8(Al,Mg,Fe)_{4-6}O_{20}(OH)_4$	$(Al,Mg,Fe)_{4-6}$	$(Al,Si)_8$	Some Si always replaced by Al. Balanced by K between layers.	K ions: strong
	Vermiculite 	Vermiculite	$(OH)_4(Mg,Ca)_6(Si_{8-x}Al_x)(Mg,Fe)_6O_{20}.yH_2O$ x = 1 to 1.4, y = 8	$(Mg,Fe)_6$	$(Si,Al)_8$	Al for Si net charge of 1 to 1.4 unit cell	Weak
2:1:1	Chlorite 	Chlorite (Several varieties known)	$(OH)_8(SiAl)_8(Mg,Fe)_6O_{20}$ (2:1 layer) $(MgAl)_6(OH)_{12}$ Interlayer	$(Mg,Fe)_6$ (2:1 layer) $(Mg,Al)_6$ Interlayer	$(Si,Al)_8$	Al for Si in 2:1 layer Al for Mg in Interlayer	
Chain Structure		Sepiolite	$Si_6O_{15}(Mg,H_2O)_8H_2O.2(H_2O)$			Fe or Al for Mg	
		Attapulgite	$(OH_2)_4(OH)_2Mg_5Si_8O_{20}.4H_2O$			Some Fe or Al for Si	Weak = chains linked by O

[a] Arrows indicate source of charge deficiency. Equivalent Na listed as balancing cation. Two formula units (Table 3.2) are required per unit cell.
[b] Electron Microscope Data.

TABLE 1 (cont'd)

Mineral Characteristics

Units:
Al-Si = 3.14 Å, Si-O = 2.65 Å, Space for Si = 0.65 Å—Thickness = 4.93 Å, C-C height = 2.1 Å.
OH-OH = 2.94 Å, Space for ion = 0.61 Å, Thickness of unit = 5.65 Å, Dioctahedral.
OH-OH = 2.94 Å, Space for ion = 0.61 Å, Thickness of unit = 5.05 Å, Trioctahedral.

Structure—Continued								Occurrence in Soils of Engineering Interest
Crystal Structure	Basal Spacing		Shape	Size[5]	Cation Exchange Capacity, meq/100 gm	Specific Gravity	Specific Surface m²/gm.	
			Irregular, somewhat rounded	.05–1 μ				Common
Triclinic a = 5.14, b = 8.93, c = 7.37 α = 91.6°, β = 104.8°, γ = 89.9°	7.2 Å		6-sided flakes	0.1–4 μ × .05–2 μ to 3000 × 4000 (stacks)	3–15	2.60–2.65	10–20	Very Common
Monoclinic a = 5.15, b = 8.95, c = 14.42 β = 96°45′	14.4 Å	Unit cell contains 2 unit layers	6-sided flakes	0.07–300 × 2.5–1000 μ	1–30			Rare
Almost Orthorhombic a = 5.15, b = 8.96, c = 43 β = 90°20′	43 Å	Unit cell contains 6 unit layers	Rounded flakes	1 μ × .025–.15 μ				Rare
a = 5.14 in O-Plane a = 5.06 in OH-Plane b = 8.93 in O-Plane b = 8.62 in OH-Plane c layers curve	7.2 Å	Random stacking of unit cells	Tubes	.07 μ O.D. .04 μ I.D. 1 μ long.	5–10	2.55–2.56		Occasional
	10.1 Å	Water layer between unit cells	Tubes		5–40	2.0 –2.2	55–70	Occasional
	9.6Å—Complete separation	Dioctahedral	Flakes (Equidimensional)	>10 Å × up to 10 μ	80–150	2.35–2.7	50–120 Primary 700–840 Secondary	Very Common
	9.6 Å—Complete separation	Dioctahedral						Rare
	9.6 Å—Complete separation	Dioctahedral	Laths	Breadth = 1/5 length to several μ × unit cell	110–150	2.2 –2.7		Rare
	9.6 Å—Complete separation	Trioctahedral		To 1 μ × unit cell breadth = 0.02 – 0.1 μ	17.5			Rare
		Trioctahedral	Similar to Mont.	Similar to Mont.	70–90	2.24–2.30		Rare
		Trioctahedral	Broad Laths	50 Å Thick				Rare
	10 Å	Both Dioctrahedral and Trioctahedral	Flakes	.003–.1 μ × up to 10 μ	10–40	2.6 –3.0	65–100	Very Common
a = 5.34, b = 9.20 c = 28.91, β = 93°15′	10.5–14	Alternating Mica and double H_2O layers	Similar ro Illite		100–150		40–80 Primary 870 Secondary	Fairly Common
Monoclinic (Mainly) a = 5.3, b = 9.3 c = 28.52, β = 97°8′	14 Å		Similar to Illite	1 μ	10–40	2.6 –2.96		Common
Monoclinic a = 2 × 11.6, b = 2 × 7.36 c = 5.32 $a_0 \sin\beta = 12.9$ $b_0 = 18$ $c_0 = 5.2$		Chain	Flakes or Fibers		20–30	2.08		Rare
		Double Silica Chains	Laths	Max. 4–5 μ × 50–100 Å Width = 2t	20–30			Occasional

References
Grim, R. E. (1968) *Clay Mineralogy*, 2d edition, McGraw-Hill, New York.
Brown, G. (editor) (1961) *The X-ray Identification and Crystal Structure of Clay Materials*, Mineralogical Society (Clay Minerals Group), London.

THE CLAY-WATER SYSTEM

It has been shown that the clay layer, made up of tetrahedral and octahedral sheets, often carries a net negative charge as a result of substitutions of certain of the cations within the sheet structure. This net negative charge results from the isomorphous substitution of cations by less positive cations. The net negative charge is often compensated by cations located on the layer surfaces. When the clay is in the presence of water, these compensating cations have a tendency to diffuse away from the layer surface. This tendency for cations to diffuse away from the layer surface in solution and yet be attracted to the layer surface due to the net negative charge gives rise to the term diffuse double layer. In a static environment, this double layer has a constant charge which is largely determined by the type and degree of isomorphous substitutions and the resulting net negative charge in the mineral layers. The understanding of the ion distribution relative to the layer surface of the clay mineral is based upon work in colloidal chemistry. When clay is dry, the adsorbed cations are tightly held to the negatively charged clay surfaces. When clay is in water, the precipitated salt associated with the cations on the particle surface goes into solution. Because the adsorbed cations are responsible for a much higher cation concentration near the surface of the particles, there is a tendency for them to diffuse away in order to provide equal concentrations throughout the liquid. The freedom or tendency to diffuse away, however, is in contradiction to the attraction force of the clay surface in the cation. Hence, an ion distribution such as shown in Figure 12 is developed. Although several theories on how this distribution of ions in the double layer can be analyzed, the most common theory used in geotechnical engineering is the Gouy-Chapman Theory. The Gouy-Chapman Theory of a diffuse double layer has been applied in attempts to explain the behavior of clays since the early 1950's. Van Olphen (1977) states that the Stern-Gouy theory is better suited to model the clay double layer than the Gouy-Chapman model. The ion distribution of other

models would provide essentially the same trends with respect to pore fluid effects; only the magnitudes would vary. Hence, for the purposes of this paper, only the Gouy-Chapman model will be considered.

Based upon the interaction of the clay minerals and the accompanying diffuse double layer under various conditions, definitions of different types of soil fabric have been developed. (See Figure 13.) The classification includes seven modes of particle association in clay suspension. These vary in limit from dispersed to flocculated. Shown in Figure 13a is a dispersed, or deflocculated, structure. The structure shown in Figure 13b is an aggregated but deflocculated structure. This structure has face-to-face association; that is, aggregations are parallel or oriented. Figure 13c presents edge-to-face flocculation with a dispersed structure. Figure 13d shows flocculation on an edge-to-edge basis, but is still a dispersed structure. Figure 13e has an edge-to-face flocculated structure of aggregated particles, while Figure 13f has an edge-to-edge flocculated structure of aggregated particles. Finally, Figure 13g has edge-to-face and edge-to-edge flocculated and aggregated particle orientation. Van Olphen (1977) defines edge-to-edge and edge-to-face particle attraction as flocculation, whereas face-to-face attraction is aggregation. Lambe (1958) says a dispersed soil is one in which the net electrical forces between adjacent particles at the time of disposition produced repulsion. If these interparticle forces were net attractive during deposition, the soil is said to be flocculated. Therefore, flocculated or aggregated structures are those in which the particles tend to join together, whereas dispersed structures are those structures in which the particles tend to move apart from each other.

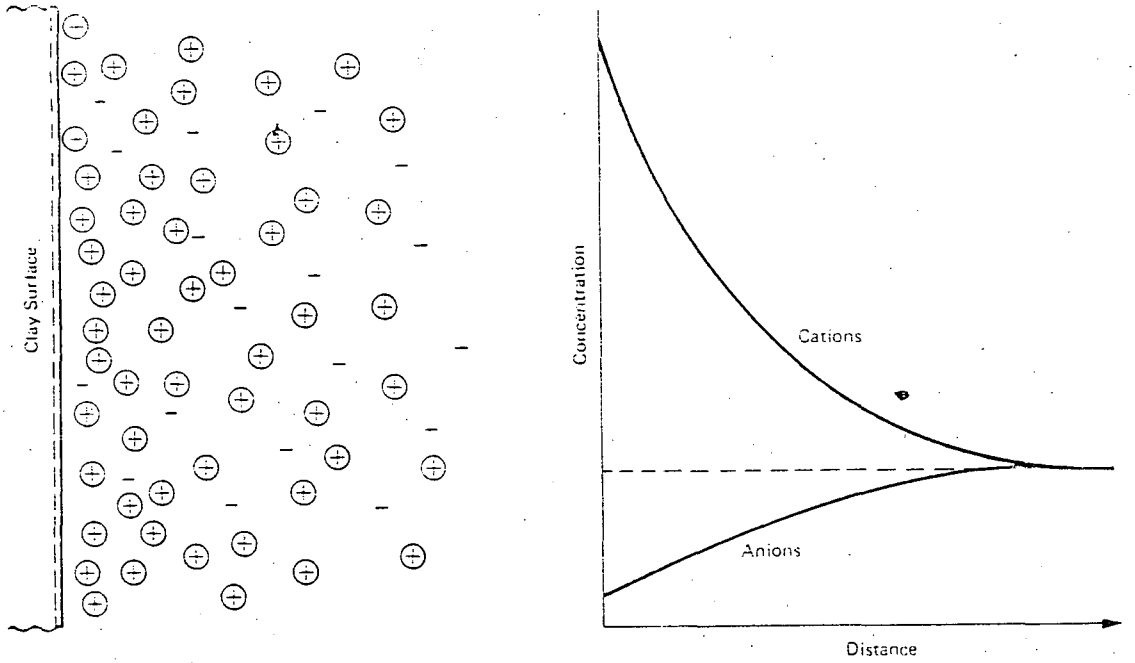


FIGURE 12 - Distribution of ions adjacent to a clay surface according to the concept of the diffuse double layer.

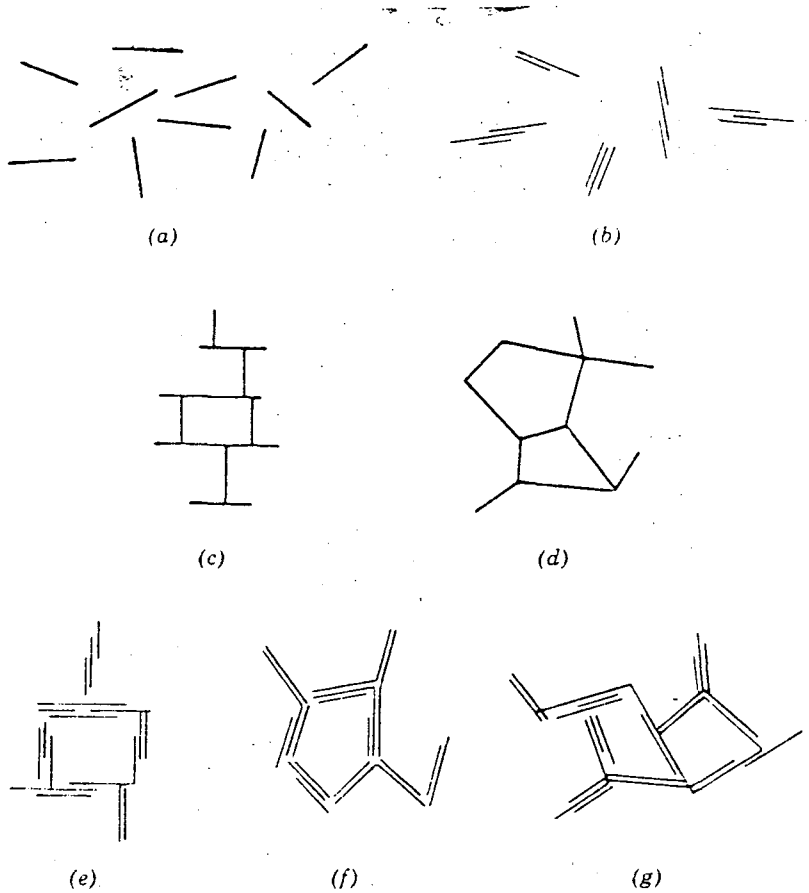


FIGURE 13 - Modes of particle association in clay suspensions, and terminology. (*a*) "Dispersed" and "deflocculated." (*b*) "Aggregated" but "deflocculated" (face-to-face association, or parallel or oriented aggregation). (*c*) Edge-to-face flocculated but "dispersed." (*d*) Edge-to-edge flocculated but "dispersed." (*e*) Edge-to-face flocculated and "aggregated." (*f*) Edge-to-edge flocculated and "aggregated." (*g*) Edge-to-face and edge-to-edge flocculated and "aggregated."

The Gouy-Chapman model tells us that the tendency toward flocculation or aggregation is usually increased by a decrease in the double layer thickness. Corresponding to the decrease in the double layer thickness is a decrease in the interparticle repulsion force. Conversely, the tendency toward dispersion is increased as the double layer thickness increases. Hence, if the double layer thickness is increased, the electrical repulsion between particles is increased, which causes the particles to disperse. The tendency towards dispersion is therefore enhanced by an increase in the double layer thickness.

In order to more fully understand the behavior of the clay-water system, and therefore the response of clays to hazardous wastes and pore fluids other than water, it is necessary to examine in more detail the variables of the Gouy-Chapman Theory and how they affect the clay structure and its behavior.

The Gouy-Chapman theory of ion distribution was incorporated into soil mechanics from colloidal chemistry theory to help explain and understand the behavior of clay-water systems. Basically, as discussed in the preceding section, a clay mineral has a net negative charge on the colloidal surface. This net negative charge causes the attraction of positive ions or cations in solution. There is an opposing tendency for the cations to be well distributed within the ionic solution due to interparticle repulsion forces. The net distribution of these cations in terms of distance from the colloidal surface is termed the diffuse double layer. These cations distribute themselves along the surface of the clay platelet, but are not permanently attached to the clay minerals. The Gouy-Chapman theory quantifies this distribution through an equation for the double layer thickness. According to Van Olphen, there are indications that, in many clays, specific adsorption forces between the layers and the cations exist. Hence, a fraction of cations

larger than that predicted by the Gouy-Chapman theory would be located on the surface of the clay particle, and a smaller fraction would be in the diffuse double layer. Therefore, the Stern-Gouy model may be more applicable to the clay double layer than the Gouy-Chapman model. However, since the Gouy-Chapman model is currently in widespread use in the soil engineering field, it is that model which will be given emphasis here.

The equation for the double layer thickness as predicted by the Gouy-Chapman theory is given as (Van Olphen, 1977):

$$t = \sqrt{\frac{\varepsilon K T}{8\pi n e^2 v^2}} \qquad (1)$$

where, t = the double layer thickness,

ε = the dielectric constant,

K = Boltzman's constant,

T = temperature,

n = electrolyte concentration,

e = elementary charge, and

v = valence of cations in pore fluid

From this equation, Lambe (1958) has presented a list of variables in the soil water system which affects colloidal stability. These are:

(1) electrolyte concentration,

(2) ionic valence,

(3) dielectric constant,

(4) temperature,

(5) size of hydrated ion,

(6) pH, and

(7) anion adsorption.

These items will be subsequently discussed in detail as they affect clay behavior.

Based on the double layer thickness and its effect on the structure of clay minerals in combination, various particle associations are defined. Lambe simply states that flocculated or aggregated structures are those structures in which the particles tend to come together. Dispersed or deflocculated structures are those structures in which the clay particles tend to move apart. A more detailed definition of these structures as given by Van Olphen is presented in Figure 13. As shown in Figure 13, structures can vary from totally dispersed or deflocculated, to aggregated but deflocculated, to edge-to-face flocculation with aggregation. Based on these particle structures, one can now examine the effect of certain variables in the clay-water system on the particle structure.

Effect of Electrolyte Concentration: An examination of Equation (1) shows that, as the electrolyte concentration goes up, the thickness of the double layer tends to decrease. The tendency towards flocculation is caused by a decrease in the double layer thickness. Hence, flocculated structures tend to be drawn together tighter and have thinner double layer thicknesses. This effect of electrolyte concentration is shown in Figure 14.

Ion Valence: Increasing the ion valence will also cause a decrease in the thickness of the double layer. With a decrease in the double layer, the tendency towards flocculation is increased. The effect of cationic valence is shown in Figure 15.

Effect of Dielectric Constant: Decreasing the dielectric constant causes a decrease in the double layer thickness and a tendency towards flocculation. The dielectric constant is a measure of a material's ability to perform as an insulator. That is,

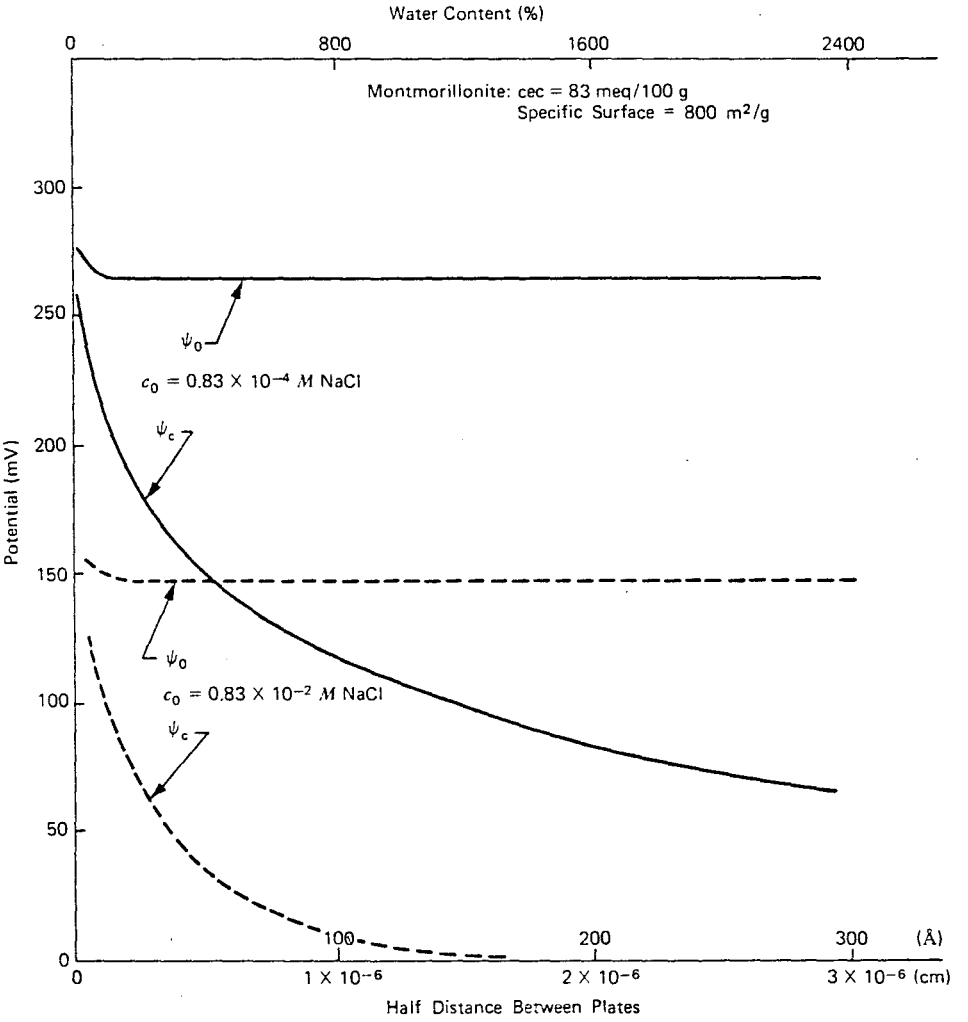


FIGURE 14 - Effect of electrolyte concentration on surface and midplane potentials for interacting parallel plates.

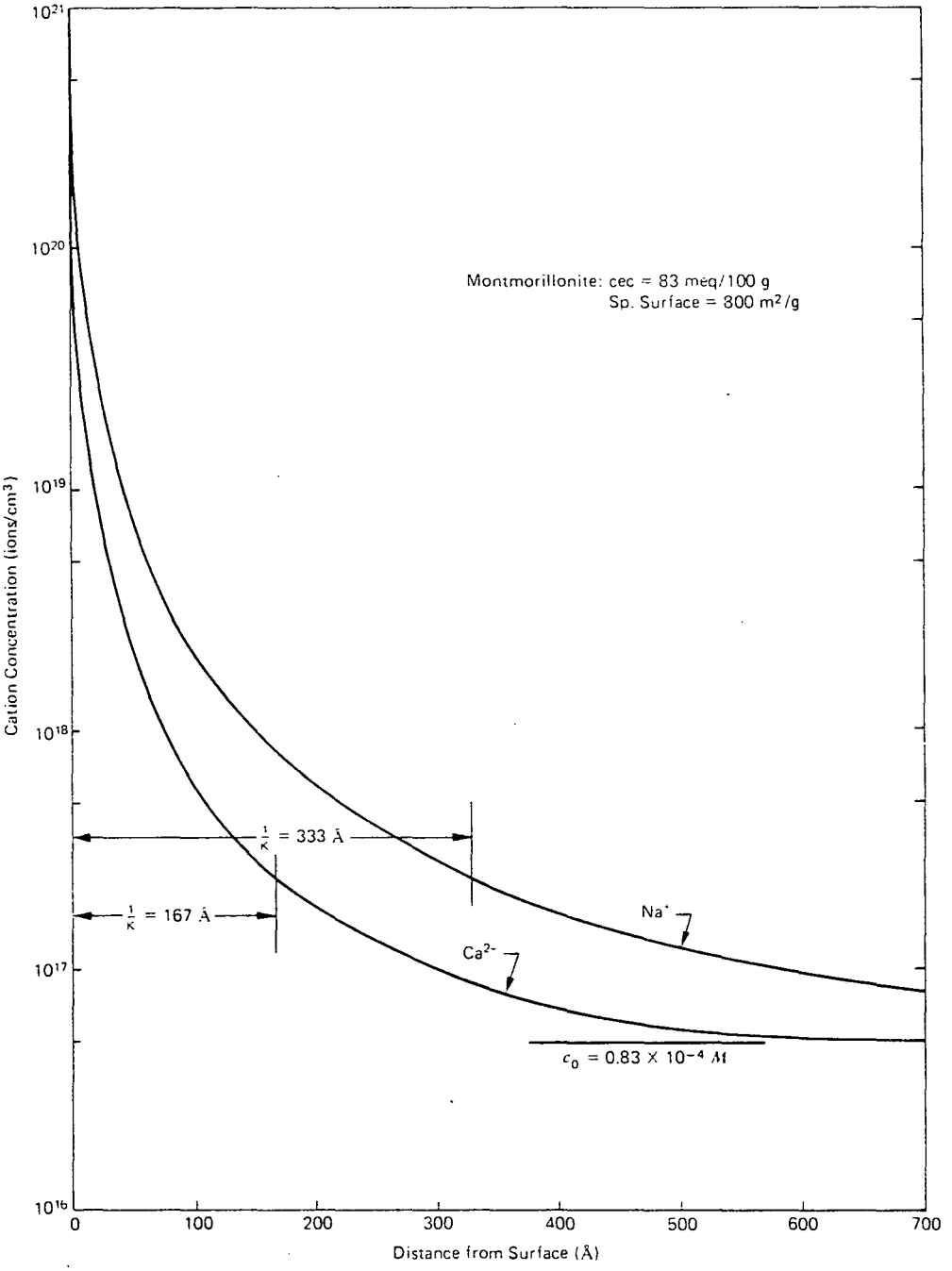


FIGURE 15 - Effect of cation valence on double layer concentrations.

it is a measure of the capacity of a material to reduce the strength of an elecric field. The higher the dielectric constant of the material, the more the material behaves as an insulator. The dielectric constant is measured in a laboratory test where two parallel plate capacitors are charged, and the potential difference between them is measured. The dielectric is inserted between them, and the potential difference is again measured. The measured potential difference is lower than the original potential difference in the vacuum. The ratio in terms of capacitance between the final capacitance and the initial capacitance is termed the dielectric constant. As this test is conducted in a vacuum, by definition, the dielectric constant of a vacuum is one. Epsilon, ε, the symbol for the dielectric constant, is also essentially one for air for all practical purposes.

Andrews, et al (1967), has noted, "... the capacity of reducing the strength of an electric field is about the same per molecule of H_2O (water) and DMSO (Dimethyl Sulfoxide) while that for DMF (Dimethyl Formamide) is about one-half the value of H_2O." This conclusion is drawn based on the value of the dielectric constant times the mole volume for each of these materials. The dielectric constants for DMSO, H_2O and DMF are 48.9, 80 and 26.6, respectively. In turn, the mole volumes for these fluids are 71.3, 18 and 77 cc's per mole, respectively. Hence, the dielectric constant times the cube route of the mole volume for DMSO, H_2O and DMF are 204, 209 and 113, respectively. The Gouy-Chapman equation clearly shows that the thickness of the double layer is strictly a function of the dielectric constant of the material, K. It is not a function of the dielectric constant per molecule. Additional study or analysis of existing data will be necessary to determine whether or not the dielectric constant per molecule is truly the controlling factor as alluded to by Andrews, et al, or simply the dielectric constant as strictly defined, as indicated in the Gouy-Chapman model.

Effect of Temperature: According to the Gouy-Chapman model, an increase in temperature causes an increase in the double layer thickness, and therefore a corresponding increase in the tendency towards dispersion. It should be pointed out, however, that many parameters are interrelated. For example, if all parameters are held constant while temperatures are allowed to increase, the double layer thickness would increase and the tendency for dispersion would increase. However, in reality, it is almost impossible to increase temperature without changing pH, and dielectric constant (Cullen, 1979). An example of this interrelationship as given by Mitchell is presented in Table 2. Hence, the product of the dielectric constant times temperature is apparently constant with reasonable changes in temperature. This is due to the fact that the dielectric constant decreases as temperature increases. This partially accounts for occasional contradictory findings reported in the literature regarding the effects of temperature on soil properties such as strength, compressibility and permeability.

TABLE 2

T(°C)	T(°K)	Dielectric Constant (D)	DT
0	273	88	2.40×10^4
20	293	80	2.34×10^4
25	298	78.5	2.34×10^4
60	333	66	2.20×10^4

Size of the Hydrated Ion: According to Lambe (1958), the smaller the ion, the closer it can approach the colloidal surface of the clay particle. Thus, the smaller the hydrated ion, the smaller the double layer and the more likely flocculation will occur in the clay particle.

The Effect of pH: The effect of pH can influence the thickness of the double layer in several ways. Changing the pH could affect the electrolyte concentration as well as the net negative charge on the clay particle by altering the extent of the dissociation of hydroxyl (OH^-) groups at the edges of the clay particle. High pH encourages the dissociation and increases the net charge, thus expanding the double layer. Low pH discourages this dissociation and causes a decrease in the net charge, therefore, causing a reduction in the double layer. As stated, a reduction in the double layer increases the tendency towards flocculation.

The Effect of Anion Adsorption: If anions are adsorbed on the clay particle, the net negative charge increases. Increasing the net negative charge causes an increase in the double layer thickness because of the increased attraction for cations. This increase in double layer thickness tends to cause dispersive clay structures.

Summary of Double Layer Influence: By an examination of the equation for the Gouy-Chapman model, the effect of pore fluid properties upon the double layer thickness has been reviewed. Further, it has been shown that a reduction in double layer thickness reduces the interparticle repulsion forces and thus increases the tendency for a flocculated or aggregated soil structure. The effects on double layer thickness and soil structures of changes in the value of any of the parameters in the Gouy-Chapman equation is shown in Table 3.

PORE FLUIDS

In order to fully investigate the effect of pore fluids on clay structure, a background into the various classes of fluids to be considered must be developed.

TABLE 3

EFFECT OF VARIOUS PARAMETERS ON DOUBLE LAYER THICKNESS AND RESULTING SOIL STRUCTURES

PARAMETER	DOUBLE LAYER THICKNESS		SOIL STRUCTURE	
	INCREASE	DECREASE	DISPERSED	FLOCCULATED
Electrolyte Concentration	Decrease	Increase	Decrease	Increase
Ion Valence	Decrease	Increase	Decrease	Increase
Dielectric Constant	Increase	Decrease	Increase	Decrease
Temperature	High	Low	Increase	Decrease
Size of Hydrated ion	Large	Small	Increase	Decrease
pH	High	Low	Increase	Decrease
Anion Adsorption	Increase	Decrease	Increase	Decrease

Note:

As shown, a change in any particular parameter (increase or decrease) has a related affect on the double layer thickness and the soil structure.

Considering the thrust of this paper toward the application aspects of clay behavior, the pore fluids will be divided following United States Environmental Protection Agency (EPA) guidelines for wastes found in industrial disposal facilities. The EPA divides these industrial wastes into four physical classes. These classes are aqueous inorganic, aqueous organic, organic and sludges. It has been estimated that 90 percent by weight of industrial hazardous wastes are produced as liquid (Cheremisonoff, et al, 1979). For the purposes of this paper, only aqueous inorganic, aqueous organic and organic wastes will be considered.

Nature of Water: Water is considered a unique solvent in several ways (Anderson & Brown 1981). It has a strong dipole moment and a high dielectric constant. Hence, the study of clay behavior normally undertaken utilizes water as the pore fluid and is significantly influenced by these two properties of water. The effect of the dielectric constant has been previously discussed. Water, a polar molecule, as a whole is electrically neutral, but has covalent bonds with shared electrons that are unsymmetrically distributed. The negative pole is located at the oxygen atom, and the positive pole is located midway between the two hydrogen atoms.

Polar molecules can be distinguished from nonpolar molecules by studying their behavior in an electric field (Masterton & Slowinski, 1969). When polar molecules are placed in an electronic field, they tend to line up with their positive poles oriented toward the negative plate and their negative poles oriented towards the positive plate. This tendency for the molecule to line up is quantified in its dipole moment. Nonpolar molecules, having no permanent centers of positive or negative charge, show little tendency to orient themselves in an electric field and are said to have a dipole moment of

zero. Dipole moments of some commonly found molecules are presented in Table 4. As shown in Table 4, water has a dipole moment of 1.84.

TABLE 4

DIPOLE MOMENTS (DEBYE UNITS)*

H_2	0	HF	2.00	H_2O	1.84	CH_3Cl	1.86
Cl_2	0	HCl	1.03	H_2S	0.92	CH_2Cl_2	1.59
CO_2	0	HBr	0.79	NH_3	1.46	$CHCl_3$	1.15
CH_4	0	HI	0.38	PH_3	0.55	CCl_4	0

* A molecule in which unit + and − charges are separated by 0.21 Å has a dipole moment of one Debye unit.

Aqueous Inorganic: Simply stated, these fluids are those in which water is the solvent, and the solute is mostly inorganic. Examples of fluids classified as aqueous inorganic are brines, caustic sodas, inorganic acids and inorganic salts.

Aqueous Organic: Wastes in which water is the solvent and the solutes are predominantly organic are classed as aqueous organic wastes. Solutes are organic chemicals such as those from wood preserving wastes, dye wastes, pesticides or ethylene glycol production wastes. It can be inferred by their water solubility that the solvated chemicals are generally polar (Anderson & Brown, 1981).

Organic: Wastes in which an organic fluid is the solvent and the solutes are other organic chemicals dissolved in the organic solvent are termed organic wastes. This class of wastes represents important liquids to be considered in the study of pore fluid effects on clays as they are frequently encountered in engineering practice. Examples of organic wastes include spent cleaning solvents, pesticide manufacturing wastes and petroleum distillates.

Organic fluids can be classified as organic acids, organic bases, neutral nonpolar fluids and neutral polar fluids.

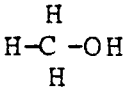
Organic acids are those organic fluids which react with bases, and include proton donors. They will likely provide cations to be adsorbed to the clay mineral surfaces, causing a decrease in the double layer thickness, according to the Gouy-Chapman model.

Organic bases are any organic fluids capable of accepting a proton to become an ionized cation. These fluids are positively charged and will strongly be adsorbed to the negative clay platelet surface. By adsorbing to the clay platelet surfaces, these fluids have a potential for causing volume changes in the clays by changing interlayer spacings as well as increasing the thickness of the diffuse double layer.

Neutral nonpolar organic fluids have essentially no charge and a small, if any, dipole moment. This group of fluids is further subdivided into aliphatic and aromatic hydrocarbons. As these fluids have essentially no charge or dipole moment, they have a potential for moving quite rapidly through the clay fabric. They also have the capability of displacing water molecules from within the hydrated clay structure.

Neutral polar compounds have essentially no charge, but exhibit relatively strong dipole moments, as compared to neutral nonpolar organic fluids. This group of fluids can further be divided into its functional group types. These group types are alcohols, aldehydes, ethers, alkyl halides and ketones. Their effect on the clay structure and fabric can be postulated based on their neutral nonpolar properties, combined with effects predicted from the Gouy-Chapman model.

In organic fluids in which the bonds to the oxygen atom in any organic molecule are all single, the substance is identified as a monofunctional alcohol. The chemical formula for a monofunctional alcohol would be C_nH_{2n+2}. In schematic fashion, alcohol is represented as:



As shown by the representative structure of alcohol, this fluid is nonpolar and neutral. Ethers are similar to alcohols with the exception that in the ether, the oxygen atom is between two carbon atoms, whereas in the alcohol, it is between the carbon atom and a hydrogen atom.

If an oxygen atom in an organic molecule is double bonded to a carbon substance, it is called either an aldehyde or a ketone. The primary difference is that the carbon in the aldehydes is shared with one carbon group, whereas in ketones, it shares a bond with two aliphatic groups. (In aldehydes, it shares a bond with one aliphatic group and one hydrogen, whereas in ketones, it shares a bond with two cations groups.)

SUMMARY

The behavior of clay on macroscopic and microscopic scales is extremely dependent upon the pore fluid. The effect of certain pore fluid properties has been discussed and is summarized on Table 3. The variability in the types of pore fluid and their properties has been reviewed.

In the final section of this paper, basics of clay mineralogy and clay structure, the concepts of the diffuse double layer theory, and the pore fluid characteristics will be tied together for the interpretation of published data involving the interaction of clays with non-water pore fluids.

PORE FLUID - CLAY INTERACTIONS

Land disposal of hazardous and sanitary wastes virtually always mandates some type of liner to protect the natural groundwater regime from the waste or the waste leachate. Typically, liners could be of clay, asphalt, rubber or another of the man-made materials such as polyvinyl chloride. Cost studies have shown that clay liners are the most cost effective, and man-made liners can frequently run ten times the cost of a clay liner (Fields & Linsey, 1975). Hence, the economic incentive for using a clay liner is strong. The understanding of the interaction between the clay liner and the liquids being retained is essential to the proper design of any such retention system.

Our present interest (1981) in the interaction of clays with various pore fluids results from our concern regarding the storage of hazardous wastes to be retained by natural clay liners. A significant contribution to our body of knowledge has been made by previous investigators considereding engineering properties of clay soil and their interaction with water. In order to better understand this interaction, they frequently compared the interaction of clay soils in pure clay mineral systems with water and other liquids. thus, we can draw upon their early studies to better understand our present problems.

Presented in this section of the report is a review of the available literature, where specific studies involving clay behavior interacting with pore fluids other than water were undertaken. This section is presented on a case study by case study basis.

MOUM AND ROSENQUIST (1961)

Two artificially sedimented and consolidated clays were prepared in the laboratory to study the effect of the mechanical properties as a function of cation replacement. Two series of illitic and montmorillonitic clays were sedimented and subsequently consolidated for a period of one year. After consolidation, half of the samples were percolated by electrolytic solutions of potassium chloride. After two years of percolation, replacement of the sodium cations with potassium cations was 60 percent complete in the montmorillonites and about 90 percent complete in the illites.

After this percolation period, the properties of the clays including water content and shear strength were studied. The water content was found to be unaffected by the cation replacement. In the case of the illites and the montmorillonites, the undisturbed shear strength was increased by the cation exchange. However, the remolded shear strength increased in the illitic clays and decreased in the montmorillonitic clays after cation replacement. X-ray diffraction revealed that the basal plane distance of the montmorillonites was reduced from 20.1 Angstroms to 16.35 Angstroms, corresponding to an expulsion of one molecular layer of water per unit cell. Considering that the total moisture content remained unchanged, this implies a transfer from adsorbed water to pore water.

These results can be examined considering what would be predicted from the Gouy-Chapman theory. By the substitution of the sodium ion by a more strongly electropositive potassium ion, the attractive forces between the cation and the negatively charged clay platelet would be increased and hence the double layer thickness would decrease. Further, the tendency for flocculation with this decrease in double layer thickness would be increased, and a corresponding increase in strength is expected.

MATSUO (1957)

As part of a larger study, the effect of sodium chloride, potassium chloride, hydrochloric acid, calcium chloride and magnesium chloride in solution upon the Atterberg limits of three Japanese soils was studied. The study included various concentrations of each of these electrolytic solutions and their effect on the liquid limit (ASTM D423), plastic limit and hence plasticity index (ASTM D424). Presented on Table 5 are the results of this testing. For the Yosaki Bay silt (MH) and the Kitishurakawa soils (ML), no clear change in the plasticity index is observed for the various concentrations of the electrolytes utilized. However, for the Yashidayama soil (CL) the plasticity index as well as the liquid limit show a marked increase for concentrations of all of the salts from 0.01 normal to 0.2 normal solutions. An increase in the liquid limit indicates an increase in the shear strength.

Examining these data in light of the Gouy-Chapman theory results in additional evidence that the Gouy-Chapman model is effective in explaining the clay behavior. The Gouy-Chapman theory dictates that, by increasing the electrolytic concentration, the double layer thickness decreases. With this decrease in double layer thickness, one would expect the shear strength to increase. This is the trend shown in Matsuo's data for the

Yashidayama soil. The trend is less pronounced, however, in the Yosaka Bay silt and the Kitishirakawa soils. The only explanation offered by the writer for this result at this time is that, with soils containing a large amout of silt-size particles, the physical-chemical effects on soil behavior are less pronounced than with colloidal soils.

LAMBE (1953)

The effect of polymers on soil properties has been studied to evaluate their potential as a soil improvement method. It was postulated that the anionic acrylate groups of the polymer strengthen interparticle bonds through the polyvalent cations present. Hence, they are highly effective in causing a flocculation tendency or a soil aggregation.

Knowing qualitatively that polymers in soil cause aggregation, it is expected that the liquid limit would increase and the permeability would decrease. As shown in Figure 16, as the percent of polymer added to the soil increased, the liquid limit clearly increased. The polymer is identified in Figure 16 as an aggregator.

TORRANCE (1975)

The role of pore fluid chemistry in the development and behavior of sensitive marine clays of Canada and Scandinavia was studied. Liquid limit tests were conducted on Leda clay using its natural pore fluid as well as electrolytic solutions of various salts including aluminum chloride, ($AlCl_3$) potassium chloride (KCl), hydrochloric acid (HCl), sodium chloride, NaCl calcium chloride (CaCl), Sodium phosphate (NaP_3O_4), calcium carbonate ($CaCO_3$), hydrogen fluoride (HF), sodium carbonate ($NaCO_3$), and sodium

hydroxide (NaOH). The results of the effect of these various electrolytic solutions at various concentrations are shown on Figure 17. It can be seen that, as the concentration of the electrolyte

TABLE 5

Sample:		*Osaka Bay silt*			*Kitashirakawa soil*			*Yoshidayama soil*		
Test:		*LL*	*PI*	pH	*LL*	*PI*	pH	*LL*	*PI*	pH
Solution										
NaCl	0·01N	73·2	34·2	7·50	49·7	17·2	4·97	44·8	19·1	4·63
	0·05N	72·5	34·5	7·61	50·3	18·3	4·50	45·8	20·2	4·70
	0·1 N	73·1	34·9	7·74	48·6	20·7	4·43	54·7	28·3	4·81
	0·2 N	77·0	37·2	7·65	45·6	17·3	4·62	61·3	37·4	5·14
	0·5 N	73·0	33·8	7·69	44·1	16·6	4·50	54·1	31·8	5·70
KCl	0·01N	76·5	35·6	7·75	53·7	23·4	4·26	43·3	19·4	5·55
	0·05N	71·0	30·0	7·48	49·5	19·1	4·12	44·8	22·2	4·95
	0·1 N	60·8	18·4	7·43	46·0	16·2	4·17	44·2	21·9	4·43
	0·2 N	68·6	26·6	7·35	45·5	16·6	4·43	55·1	32·6	4·35
	0·5 N	71·3	31·5	7·53	46·0	17·0	4·70	55·5	31·7	5·33
HCl	0·01N	81·0	39·2	7·45	47·9	15·6	4·82	52·3	30·0	4·54
	0·05N	79·6	39·4	7·41	53·1	21·2	4·34	57·3	29·3	4·26
	0·1 N	74·9	34·1	7·41	56·4	25·6	4·17	53·0	25·7	4·09
	0·2 N	77·3	34·8	7·41	53·2	21·3	3·91	52·7	29·1	3·91
	0·5 N	78·0	38·0	7·61	48·6	17·6	3·21	51·7	33·5	3·83
$CaCl_2$	0·01N	74·1	34·2	7·43	44·8	15·4	5·16	50·8	20·0	6·02
	0·05N	69·0	28·4	7·57	45·0	15·8	4·82	51·4	21·7	4·64
	0·1 N	73·6	33·9	7·57	50·1	20·5	4·63	56·3	31·1	4·42
	0·2 N	76·1	32·8	7·57	47·7	18·7	4·47	54·6	36·9	4·64
	0·5 N	74·5	31·5	7·61	48·6	20·0	4·99	57·0	35·0	4·96
$MgCl_2$	0·01N	74·0	32·4	7·40	44·5	16·9	4·34	45·8	17·4	7·15
	0·05N	74·0	31·4	7·59	44·5	17·0	3·42	48·6	20·2	5·05
	0·1 N	75·2	32·8	7·38	46·7	19·2	4·52	49·2	24·4	4·63
	0·2 N	74·0	33·0	7·23	41·8	13·2	4·82	57·3	33·1	4·60
	0·5 N	71·0	30·6	7·10	46·5	18·6	5·16	49·1	27·7	4·95

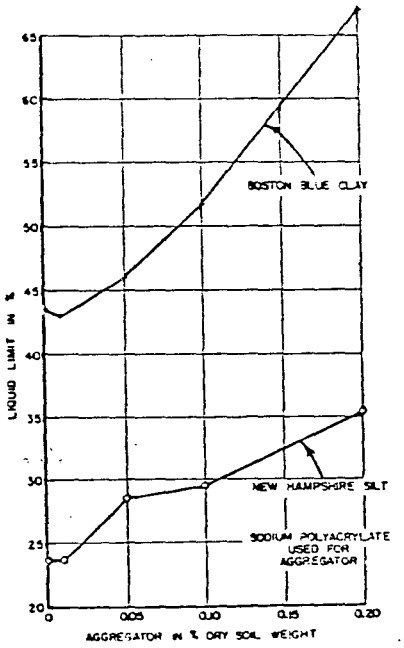


FIGURE 16 - Effect of aggregator on liquid limit.

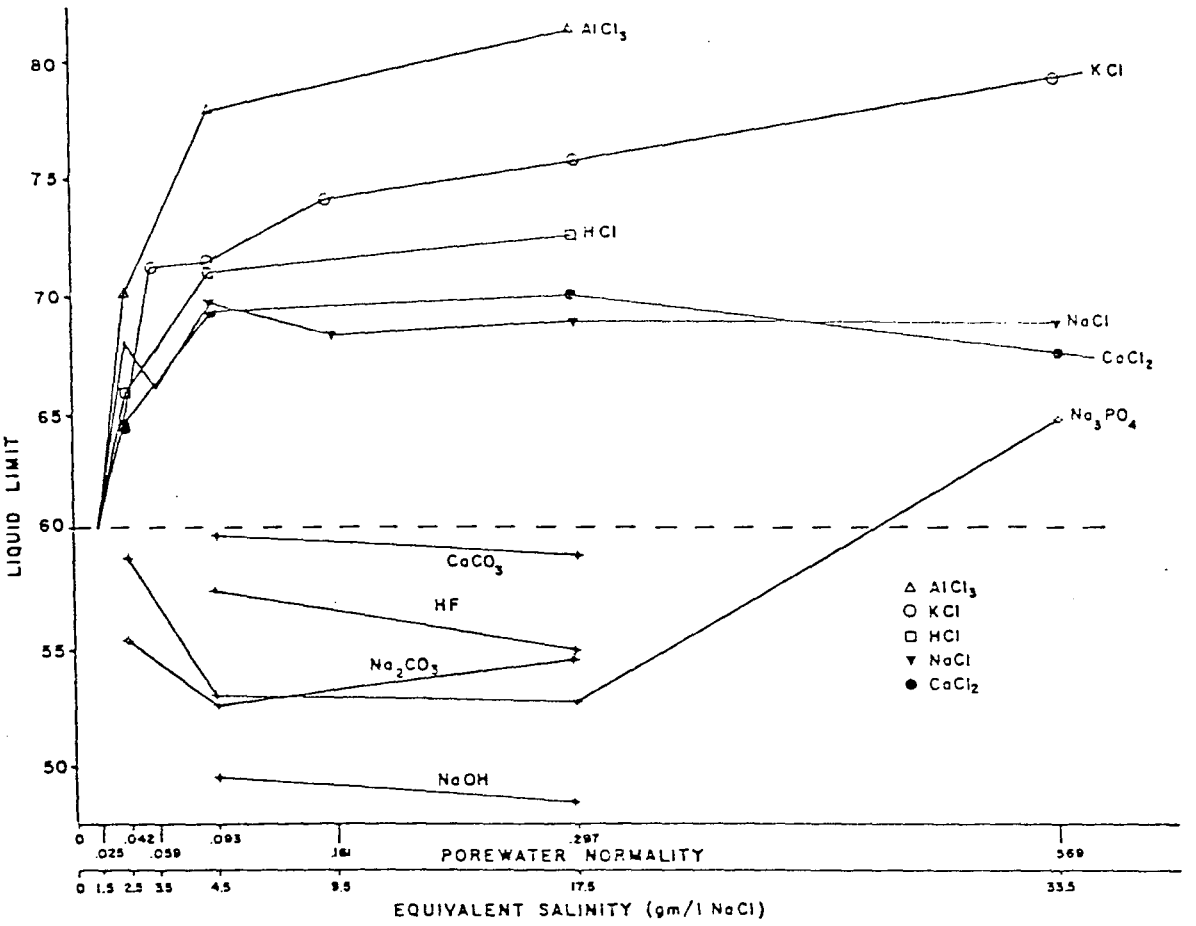


FIGURE 17 - The influence of various salts on the liquid limit of Leda clay from the Heron Road - Bronson Avenue interchange in Ottawa.

in solution increases, the liquid limit generally increases. As previously discussed, this is compatible with the predictions of the Gouy-Chapman theory, which would indicate a decrease in the double layer thickness and an increase in the tendency towards flocculation with an increase in electrolytic concentration. However, there seems to be a saturation type level, as the effect is quite pronounced at low concentrations, but apparently levels off at higher concentrations. This tendency could provide additional insight to the scatter in the data by Matsuo at higher electrolyte concentrations. Also note that, as the cation becomes more polar, the effect is to increase the liquid limit at any given concentration. Again, this is to be expected based on the Gouy-Chapman model.

VEES AND WINTERKORN (1967)

In this study, Vees & Winterkorn prepare four clay samples as homoionic clays. In this way, they can study the effect of cation exchange on the various soil properties. In order to prepare, in the author's terms, the "homoionic modifications", a ten-liter aqueous solution containing ten times the quantity of cations required for base exchange within the clay mineral was made. The powdered clays were then added slowly to a mixer, and the resulting dispersion was mixed for two days. The solution was then left to rest for a period of seven days prior to decanting the supernatant.

After completion of the homoionic modifications, a series of experimental tests were carried out. These tests included:

(1) liquid limit, plastic limit and plasticity index;

(2) sorption tests;

(3) consolidation tests; and

(4) shear tests of saturated samples.

The results of the plasticity properties are presented in Figure 18. It can be seen that, depending upon the primary ion, both the liquid limit and the plastic limit vary. In the kaolinite, for example, the plastic limit varied from 31 to 42, depending upon the primary ion. In like manner, the liquid limit varied from 58 to 68. It is noted, however, that for the case of kaolinite, the plastic limit varied only slightly from 25 to 29. This was not the case in the bentonite. For kaolinite, the plastic limit increases with increasing electropositivity of the exchange ion. This indicates an increasing flocculation effect for the clays containing a large base exchange capacity and an extreme tendency for dispersion. A pseudo structure may be formed by the addition of water. Each particle wants to adsorb all the water it can.

The results of the water sorption tests for the kaolinite are shown on Figure 19. It has been previously shown that the permeability depends on the total porosity, the dispersive or flocculative structure of the secondary aggregations, the rate of destruction of interparticle bonds by capillary water, and the type and amount of water bonding to the surfaces of the mineral particles (Winterkorn & Choudhury, 1949). The rate of water sorption depends primarily upon the effect of permeability while the ultimate volume of sorbed water is the measure of the type and degree of water interaction with the clay mineral surfaces. Thus, the Th-clay shows the highest initial sorption rate and the lowest ultimate intake. Based on its flocculated structure and its low water affinity, this is expected. Considering the low cation base exchange capacity of kaolinite, the observable ion effect is apparently influenced by the type of secondary structure rather than by the

individual water affinities of the ions themselves.

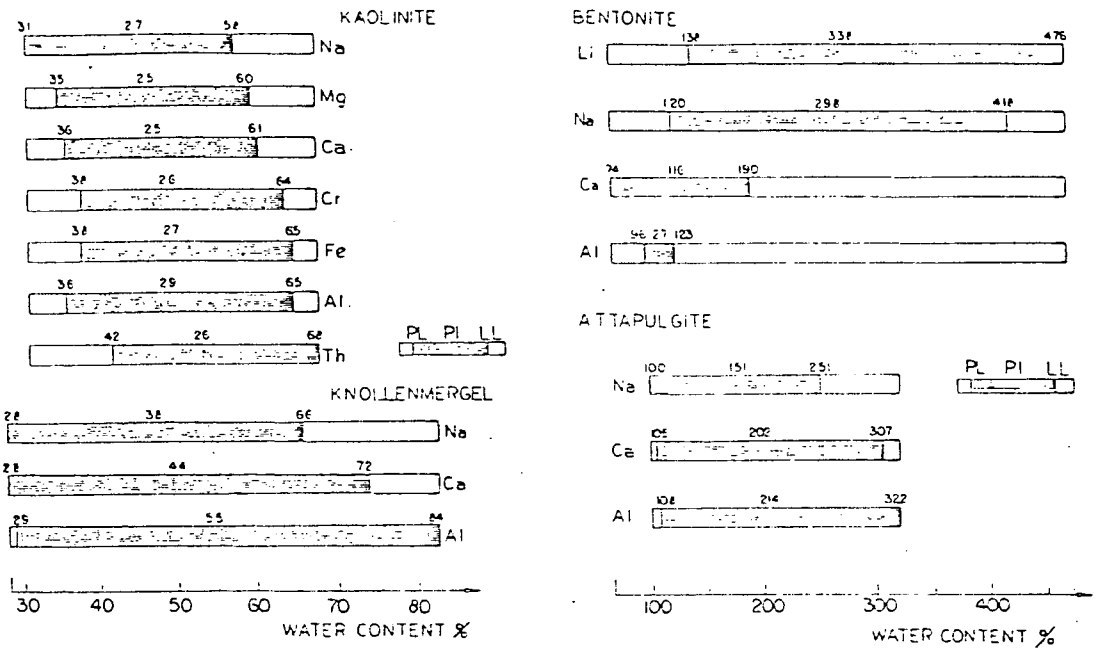


FIGURE 18 - Consistency properties of the homoionic modifications of kaolinite, knollenmergel, bentonite and attapulgite.

The coefficient of permeability was calculated from consolidation test results for each of the homoionic modifications. These results are presented on Figure 20. These data show the influence of valence of exchange ions in the case of attapulgite and bentonite. It is also evident in the knollenmergel and kaolinite. Presented on Figure 21 is a plot of the shear strength versus void ratio for several of the homoionic modifications. It is clearly seen that the shear strength is influenced by the valence of the exchange ions.

LEONARDS & ANDERSLAND (1960)

Shear strength tests evaluating the effects of temperature and electrolyte concentration yielded results contrary to those predicted by the Gouy-Chapman theory.

An increase in salt concentration according to colloidal theory reduces the thickness of the double layer, thereby decreasing the repulsive force between particles. This should result in a more flocculated clay structure and hence a higher shear strength. A study relating undrained shear strength and salt concentration yielded the opposite results. As the salt concentration increased, the strength decreased as shown in Figure 22. Similarly, colloidal theory predicts an increase in shear strength with a decrease in temperature. As shown in Figure 22, this relationship was found to hold.

LEONARDS & GIRAULT (1961)

In a study of the one-dimensional consolidation test, the effect of pore fluid on the compressibility of undisturbed samples of Mexico City clays was examined. In this study, the naturally occurring pore water was replaced with carbon tetrachloride (CCl_4) by circulating the pore fluid through the sample until the effluent was pure carbon tetrachloride.

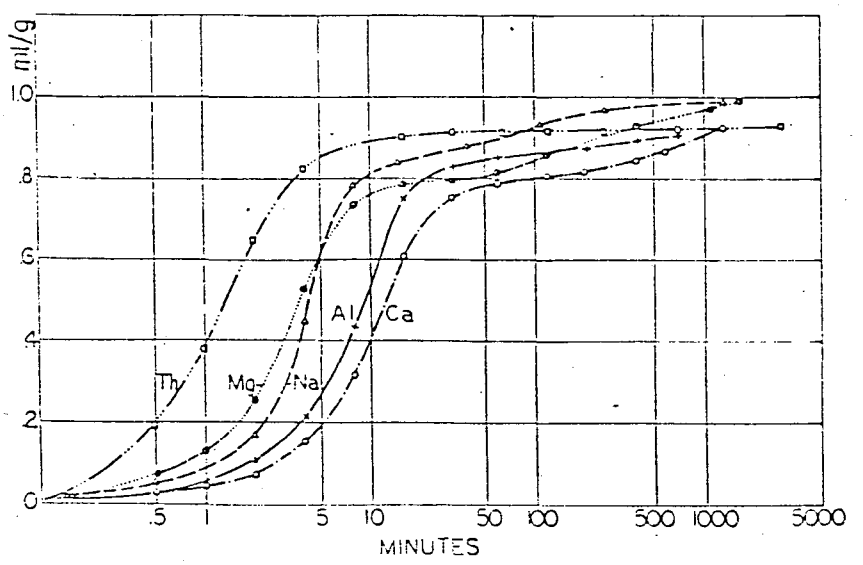


FIGURE 19- Water sorption of kaolinite as a function of type of exchange ions and time.

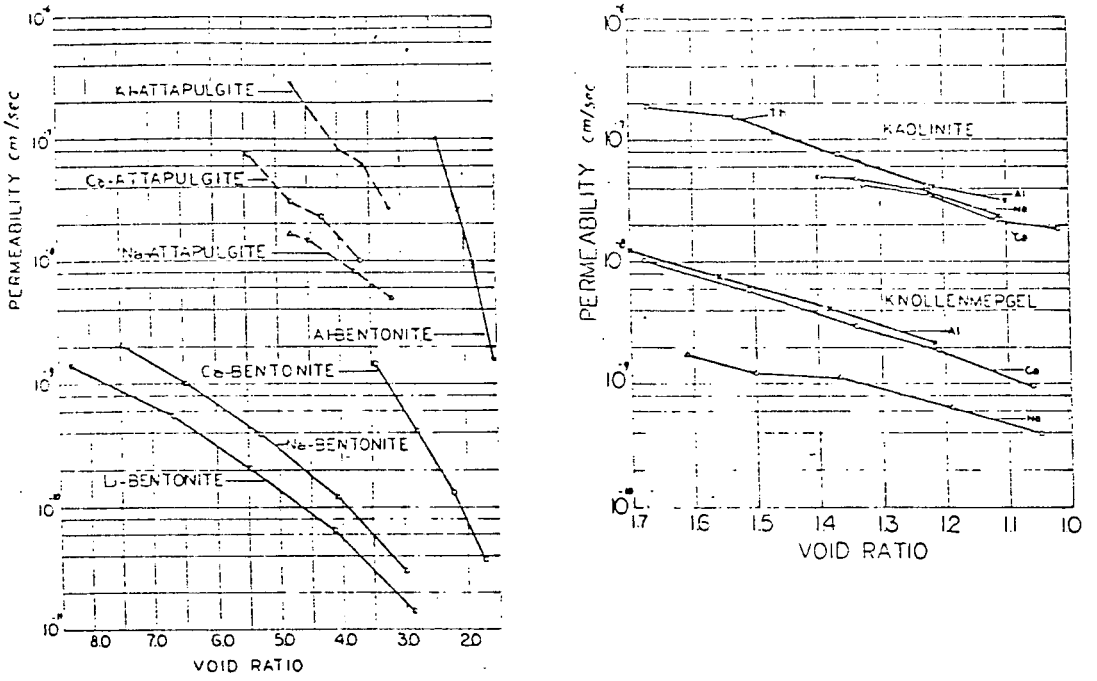


FIGURE 20- Permeability coefficient of attapulgite, bentonite, kaolinite and knollenmergel as a function of exchange ion type and void ratio.

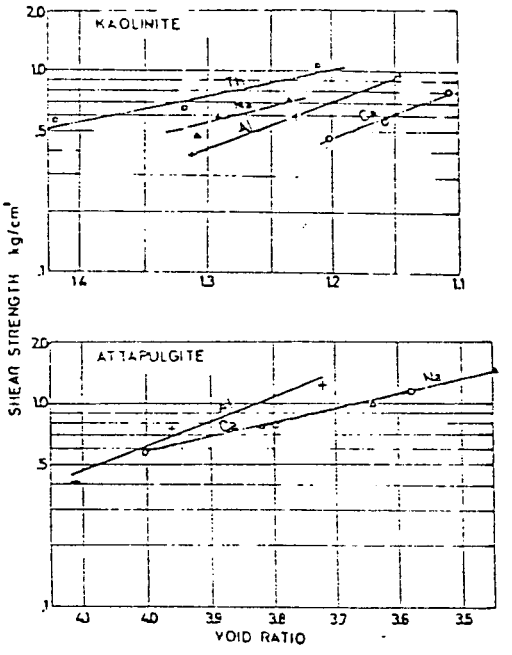


FIGURE 21- Shear resistance of overconsolidated homoionic kaolinite and attapulgite specimens as a function of void ratio calculated from actual water contents of saturated specimens.

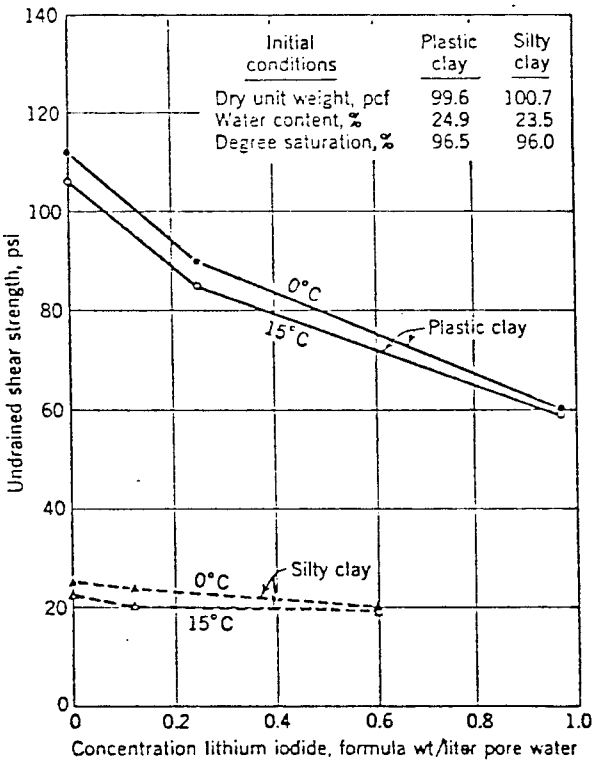


FIGURE 22 - Effect of salt concentration on undrained shear strength. (from Leonards and Andersland, 1960)

The investigators found that the alternate pore fluid significantly affected compressibility. First, there was an overall decrease in the compressibility of the Mexico City clay with the nonpolar carbon tetrachloride. Secondly, there was a substantial increase in the observed preconsolidation pressure. An overconsolidation ratio of two was measured on this normally consolidated clay after the introduction of carbon tetrachloride as a pore fluid. It was concluded that a normally consolidated clay can exhibit apparent preconsolidation pressures due to changes in the interparticle forces.

This increase in the overconsolidation ratio can be examined in light of the Gouy-Chapman theory. As previously presented, colloidal theory predicts that the total repulsion force between particles decreases as the dielectric constant decreases. Carbon tetrachloride has a very low dielectric constant, and it would therefore be expected that the interparticle forces would be greater with this pore fluid than with the naturally occurring pore water. If the total repulsion force between particles decreases, one would expect higher interparticle bonding and hence a higher apparent preconsolidation pressure. The results of this study are therefore consistent with those predicted by the Gouy-Chapman theory.

GRIFFIN, R. A., ET AL. (1976)

A series of laboratory leachate tests were conducted in order to evaluate the potential of various clay minerals for attenuating chemical constituents. The test utilized leachate from a sanitary landfill permeating kaolinitic, illitic and montmorillonitic clays in a matrix of quartz sand. Prior to permeation, the clay mineral structures were analyzed by X-ray diffraction in order to evaluate the exchangeable ions. The leachate was chemically analyzed before and throughout the ten-month testing program. At the completion of the testing, the soil samples were sectioned and analyzed to determine the chemical distribution through the samples. The study found that chloride, sodium and water-soluble organics were relatively unattenuated. Potassium, ammonium, magnesium, silicon and iron were moderately attenuated. Finally, the heavy metals - lead, cadmium, mercury and zinc - were strongly attenuated. Conversely, calcium, boron and manganese were significantly higher in the effluent concentration than in the original leachate. Montmorillonite was more effective in attenuating the chemical constituents, followed by illite and kaolinite. This trend is consistent with that predicted from the physical-

chemical standpoint in relation to clay mineralogy. The increase in effectiveness in attenuating chemical constituents is directly related to the cation exchange capacity of the clay mineral. The principal attenuation mechanism was identified to be precipitation for the metals and cation exchange for the other chemical constituents attenuated. Finally, the hydraulic conductivity or permeability was found to decrease with increasing time during the testing period.

FULLER (1978)

In a similar study to that conducted by Griffin, et. al. (1976) leachates were utilized to permeate 11 different naturally occurring clayey soils. The leachate was generated in a homeowner type septic tank, and at times spiked with various chemical constituents. Soils were analyzed to evaluate their clay mineralogical structure prior to permeation. The results in this study were in contrast to those found by Griffin. The investigator found that the types of clay minerals and the cation exchange capacity were among the least important factors in the attenuation of chemical constituents from the leachate. The amount of clay in the soil sample, however, was considered to be the most important factor. Since the hydraulic conductivity will generally decrease with increasing clay fraction, the results would suggest that a lower hydraulic conductivity with the accompanying increase in clay content would be more effective in the attenuation of chemical constituents in the leachate.

These results are somewhat consistent with those that would be predicted from colloidal theory. It is clear, based on the study conducted by Griffin, et. al. 1976 and our knowledge of clay mineralogy, that the cation exchange capacity is an important factor in the attenuation of chemical constituents in leachate. However, it is also clear

that increasing the clay fraction, and thus the overall capacity for cation exchange within a given volume of material, would also significantly affect the attenuation of chemical constituents in the leachate. In the writer's opinion, the study by Fuller included enough variability in the clay content of the leached samples to mask that effect of clay mineral structure and cation exchange capacity.

ANDREWS, GAWARKIEWICZ & WINTERKORN (1967)

The study was undertaken to compare the interaction of three clay minerals with three pore fluids. The pore fluids were water (H_2O), dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF). The clay minerals used were kaolinite, attapulgite and sodium montmorillonite. The properties of the liquids are presented in Table 2. Both DMSO and DMF are aprotic solvents. Their polar nature is shown by the dielectric constants and dipole moments shown in Table 6. As previously discussed, when considering the dipole moment as well as the mole volumes, it is computed that the dielectric constant times the cube root of the mole volume is approximately the same for H_2O and DMSO. The authors point out that in DMSO and DMF molecules, the positive end of the dipole is not accessible as is the case with H_2O. This shielding makes the interaction of the dipoles with anions considerably weaker than with cations. Therefore, the dissolved anions and anionic surfaces are relatively free from interaction with the

Property	Water	DMSO	DMF
Formula	H_2O	$(CH_3)_2SO$	$(CH_3)_2HCON$
Specific gravity (20 C/20 C)	0.99823	1.1008	0.950
Molecular weight	18.00	78.13	73.09
Melting point, deg C	0.0	18.45	-61.0
Boiling point, deg C, at 760 mm Hg	100.0	189.0	153.0
Liquid range, deg C, at atmospheric pressure	100	170.55	214.0
Specific heat, cal/g	1.0	0.47 (29.4 C)	0.5 (20 C)
Mole heat, cal/mole	18.0	36.7	38.6
Mole volume, cc/mole	18.0	71.3	77.0
Heat capacity, cal/cc	1.0	0.517	0.475
Average atom heat, cal/atom	6.0	3.67	3.05
Surface tension, dyne/cm	72.75	42.95	35.2
Molar surface energy, erg	495	737	637
Viscosity, centipoise (20 C)	0.894	1.98	0.802
Refractive index	1.33 (20 C)	1.4783 (20 C)	1.4269 (25 C)
Dielectric constant	80.00 (20 C)	48.9 (20 C)	28.6 (25 C)
Dipole moment, Debye units	1.89	3.9	3.85
(Dielectric constant) × (mole volume)$^{1/3}$	209	204	113

TABLE 6

PROPERTIES OF THE LIQUIDS EMPLOYED

liquid while cations can become solvated. Since the solid surfaces of clay minerals in aqueous solutions are predominantly negatively charged or anionic in character, this property of DMSO and DMF molecules is of particular interest.

In order to study the effect of these various pore fluids on the three clay minerals, an extensive testing program was undertaken. Tests included specific gravity and specific volume, Atterberg limit tests, the Dietert compaction tests, sorption tests, sedimentation volumes, and cracking patterns of thin clay slurry films. The authors note that the specific volume, which is the inverse of the specific gravity of clay in a particular liquid depends upon the specific volume of the clay substrate, the weights and volume of the exchangeable ions on the clay, the interaction between the exchangeable ions and the clay particles in the wetting liquid, the interaction between the clay substrate and the wetting liquid, and the dried clay crumbs or the sizes of the pores in the clay crumbs. These factors were utilized in the evaluation of the data obtained from their tests. The Atterberg limit test determines the moisture contents at which changes of state from liquid to plastic to semisolid to solid occur. The position of these limits on a moisture scale is based upon the water affinity of the mineral components of the clays, their tendency to form secondary and higher structural units, and their granular composition, which controls packing properties and pore space geometry. The Dietert compaction test is an impact compaction test utilizing smaller samples than the standard Proctor compaction test. Sorption tests are a measure of the clay's propensity to take on fluid. The determination of sediment volumes, frequently used in colloidal chemistry, is little used in soil engineering. In general, flocculated particles settle rapidly to high equilibrium values while deflocculated particles settle slowly to low equilibrium values. The test is usually performed by dispersing a known amount of solids in a large excess of liquid to determine the relative rate of settling and the final volume of sediment. Cracking patterns of thin clay slurry films are an indication of the tensile stresses set up by the clay minerals as they lose their liquids by evaporation.

It was found that the specific volume of kaolinite and attapulgite was relatively unaffected by the change in pore fluids between H_2O and DMSO. However, the specific volume of the sodium montmorillonite was significantly greater in water than in DMSO. The results of the Atterberg limit test are presented in Table 7. When compared to water, the plasticity index for DMSO was higher for the kaolinite but lower for the attapulgite and sodium montmorillonite. The most profound effect on plasticity was with the sodium montmorillonite where the plasticity index was lower for DMSO than water by a factor of 7.5.

The results of the Dietert compaction test, consistent with the previous tests showed only minor effects of alternate pore fluids with kaolinite and attapulgite. Whereas, with bentonite, significant effects were observed. In all cases, a larger maximum density was obtained with water than with DMSO. For both the kaolinite and bentonite, the optimum liquid content was higher for DMSO than it was for water. Conversely, for attapulgite, the optimum liquid content was higher for DMSO than it was for water, indicating the additional elasticity of the attapulgite mineralogical system.

TABLE 7 - ATTERBERG LIMITS

Clay	Liquid	LL	PL	PI	$\frac{PI\ H_2O}{PI\ DMSO}$	SL
Kaolinite	H_2O	62	33	29	0.53	29
	DMSO	105	50	55		
Attapulgite	H_2O	291	110	181	1.17	80
	DMSO	309	155	154		
Na-Bentonite	H_2O	506	55	451	7.5	6
	DMSO	140	80	60		

For all clays except kaolinite, the final sorption data were higher for water than for DMSO. Further, the sorption ratios are higher for bentonite than for attapulgite.

The sorption values for kaolinite, being higher for DMSO than water, indicate a greater affinity for DMSO than for water of the kaolinite mineral structure.

The sedimentation test yielded the following ratios for H_2O:DMSO:DMF, respectively:

Kaolinite - 0.63 : 1 : 0.64

Attapulgite - 2.6 : 1 : 0.65

Bentonite - Infinity : 1 : 1.08

From these data, one can see that kaolinite interacts more strongly with DMSO than either water or DMF. Bentonite interacts most strongly with water, but to about the same degree with both DMSO and DMF. Attapulgite interacts most strongly with water, followed by DMSO and least with DMF. The stronger interaction of kaolinite with DMSO and DMF than with water is consistent with the sorption data which showed the Kaolinite had a greater affinity for the organic solvents than for water.

The cracking patterns of thin slurries were observed for all three clay minerals. The drying of the kaolinite film produced no cracking pattern. However, the film produced by DMSO has the smoothest appearance, indicating its great interaction between the DMSO and the kaolinite. The attapulgite water film showed a few cracks, forming relatively large structural units indicating a relatively large tensile strength of the clay-water system and good mobility of the clay particles at relatively low water contents. Finally, the bentonite water films produced no cracks, whereas the bentonite-DMSO system produced a cracking pattern of a larger scale than that with DMF.

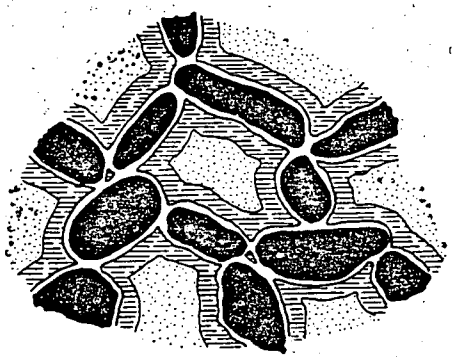
The authors present the conclusions relating to the above data in order to better understand the fundamental behavior of clay minerals. They conclude that, since plasticity index values are taken as a measure of the interaction between the mineral surfaces and the liquids, then this interaction in the water system was, as expected, greatest with bentonite and least with kaolinite. With DMSO, however, the absolute plasticity index value was greatest for attapulgite and much less for both bentonite and kaolinite. Further, the plasticity index value for kaolinite with DMSO was about twice that with water. The great difference in the interaction of DMSO with kaolinite and bentonite, respectively, with attapulgite lying in between emphasized the marked differences in the respective surface characteristics and probably the manner in which the water molecules are associated with these surfaces. The very strong interaction of DMSO with kaolinite showed itself in all of the tests.

SKEMPTON & NORTHEY (1952)

In an effort to understand sensitivity of clays, a study was undertaken investigating in the effect of leaching upon remolded shear strength. It was found that very high values of sensitivity could only be obtained with samples that were originally formed from clay-water slurries with a high salt concentration and then subsequently leached. It was found that heavily overconsolidated clays and fresh water lacustrine clays exhibited sensitivities in the low to medium range. High sensitivities were only found in marine clays which have evidence of subsequent leaching and reduction in salt concentration. The data the authors present for this conclusion is overwhelming.

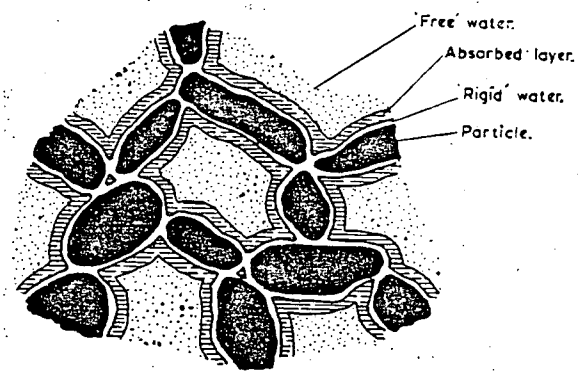
In an effort to understand the effective leaching on the clay behavior, the authors considered the physical-chemical properties of the clay minerals. The authors

attribute the great strength reduction upon remolding, and hence, the high sensitivity to what they term the "meta-stable structure in marine clays." Shown on Figure 23, the clay structure is basically made up of the clay particle, the (bound) water and the free water. In interpreting the authors' work, the writer concluded that the bound water the authors refer to is that water adsorbed to the clay platelet and found within the diffuse double layer. Considering the concentration of salts in the pore water, the thickness of the diffuse double layer is rather large. Although not referenced by the author, this is in agreement with that predicted by the Gouy-Chapman model. After leaching, a change in salt concentration would cause a reduction in thickness of the diffuse double layer and hence, given no change in moisture content, an increase in the free water as shown in Figure 24. Considering the new structure after leaching and the increase in the



(a) BEFORE LEACHING.

Figure 23 Effect of leaching on undisturbed marine clay



(b) AFTER LEACHING.

Figure 24 Effect of leaching on undisturbed marine clay

proportion of free water, it would be expected that the remolded strength would be very much lower in the leached clay than that in the clay before leaching. This hypothesis for the documented behavior is offered by the authors in a qualitative manner. Clearly, the explanation is compatible with the behavior predicted by the Gouy-Chapman theory.

ROSENQUIST (1952)

Considerable investigatory work pertaining to the formation and behavior of Norwegian quick clays was undertaken in the 1940s and early 1950s. As a result of these studies, the effect of salt concentration or electrolyte concentration upon clay behavior was considered among many other factors. It is the effect of electrolyte concentration on clay behavior that is of interest herein.

Increasing the electrolyte concentration in the pore fluid has been shown to increase the liquid limit of the soil. The liquid limit is a measurement of a clay's remolded shear strength. It is a measure of the water content at which, under a given energy, a given type of shear failure occurs. Hence, if the liquid limit increased with increasing electrolyte concentration, it meant, for that shear failure to occur in the soil, a higher moisture content was required with a higher electrolyte concentration. Recall that, as the electrolyte concentration increases, the thickness of the diffuse double layer tends to decrease. From these two facts, the writer concludes that a decrease in diffuse double layer thickness will cause an increase in the liquid limit of the soil.

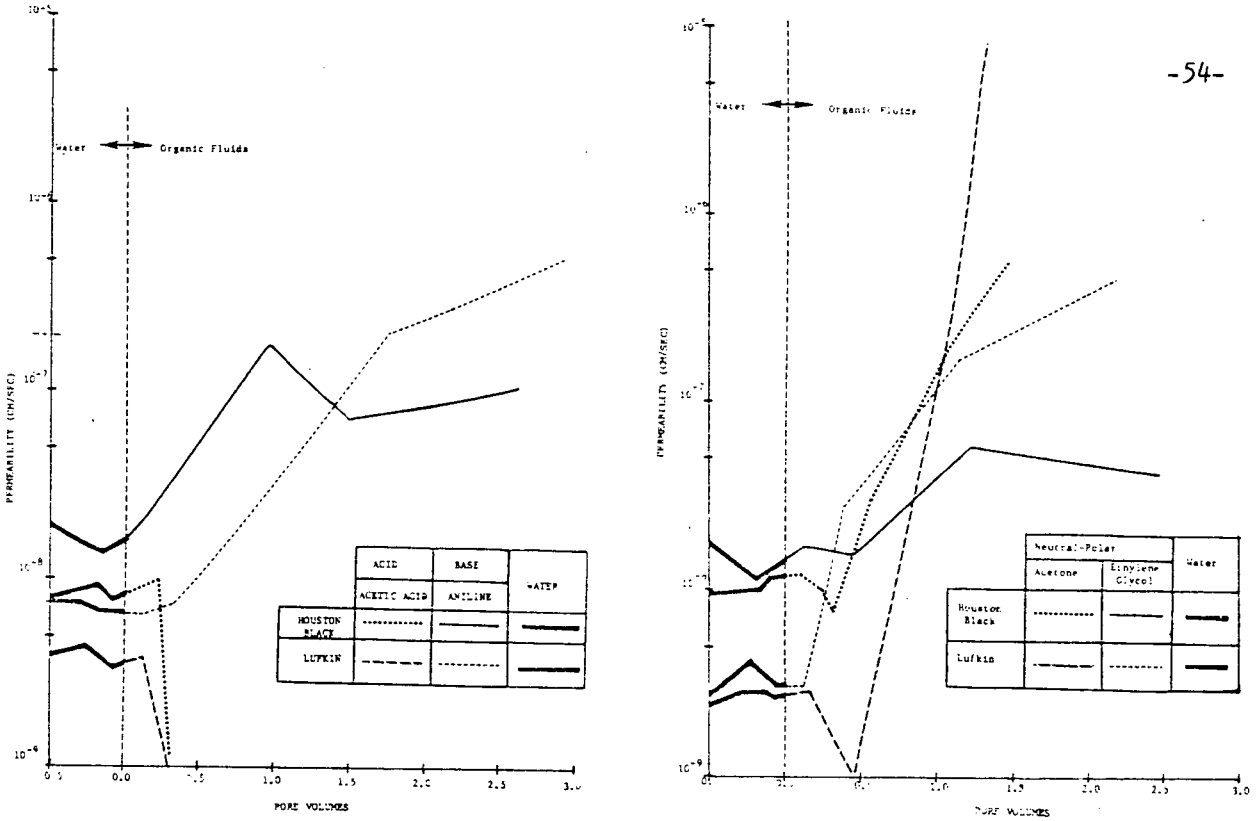
The author's studies also show that the plastic limit remains essentially unchanged after pore fluid electrolyte concentration changes are introduced.

ANDERSON & BROWN (1981)

A study was undertaken in which two smectite clay minerals were permeated with organic fluids in what was considered a standard permeability test procedure. The permeants were acetic acid, analine, acetone, ethylene glycol, heptane and xylene. The physical and chemical properties of these permeants are presented on Table 8. The results of these permeability tests are presented on Figure 25. The Lufkin clay soil consists of a soil with approximately 48 percent clay minerals and a total cation exchange capacity of 24. The Houston black has about 56 percent clay and a cation exchange capacity of 33. The authors note that acetic acid caused decreases in permeability in both soils. However, there was a significant amount of soil piping occurring in the two acid impermeated cores, as evidenced by the presence of soil particles in the leachate. Analine, a base, treated course showed substantial permeability increases with time. The acetone treated course showed an initial decrease followed by large increases in permeability. In summary, significant increases in permeability were obtained with basic neutral polar and neutral nonpolar organic fluids over those values obtained with water.

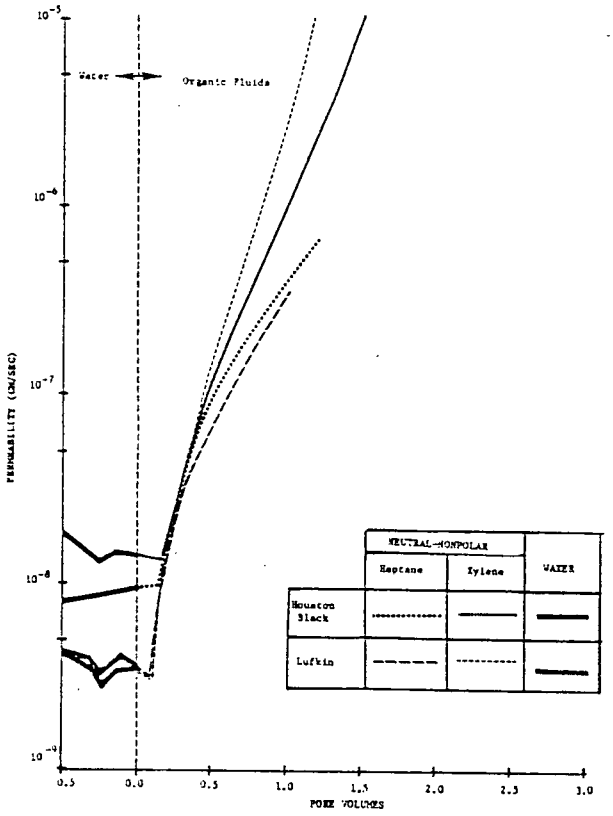
TABLE 8
PHYSICAL AND CHEMICAL PROPERTIES OF THE PERMEANTS TESTED

PERMEANTS		Water Solubility (gm/l)	Dielectric Constant		Dipole Moment	Temp. Range of the Liquid State (°C)		Viscosity (Centipoise)		Density (g/cm^3)	Molecular Weight
Organic Fluids	Name	@ 20° C	@ 20°C	@ 25°C	(debyes)	Freezing	Boiling	@ 20°C	@ 25°C	@ 20°C	
Acid, Carboxylic	Acetic Acid	∞	6.1		1.74	17	118	1.28	1.16	1.05	60
Base, Aromatic Amine	Aniline	34.0	6.9		1.55	-6	184	4.40	3.71	1.02	93
Neutral-Polar, Acetone	Acetone	∞		20.7	2.90	-95	56	0.33	0.32	0.79	58
Neutral-Polar, Glycol	Ethylene Glycol	∞	38.66		2.28	-13	198	21.0	17.3	1.11	62
Neutral-Non Polar Aliphatic	Heptane	0.003	1.0		0.00	-91	98	0.41	0.39	0.68	100
Neutral-Non Polar Aromatic	Xylene	0.20	2.5		0.40	-47	137	0.81	0.62	0.87	106
Water			80.4	78.5	1.83	0	100	1.0		.98	18



(a) (b)

FIGURE 25 - Permeability of Houston black and Lufkin clay soils to (a) acetic acid and aniline, (b) acetone and ethylene glycol, and (c) heptane and xylene.



(c)

From this the authors conclude that the need to test the permeability of clay liners with actual leachates is especially important where organic fluids may be in the waste.

Considerable time was spent by the authors in their paper describing the test method for determining the effects of waste leachate on the permeability of compacted clay soils. In essence, their tests are conducted in a compaction mold permeameter as shown in Figure 26. Although they use a rather high pressure, indicating a significant gradient, no backpressure or consolidation pressure is utilized. Clearly, trapped air is a common cause for artificially low permeability values and, in order to provide adequate precaution against the entrapment of air, a backpressure is required.

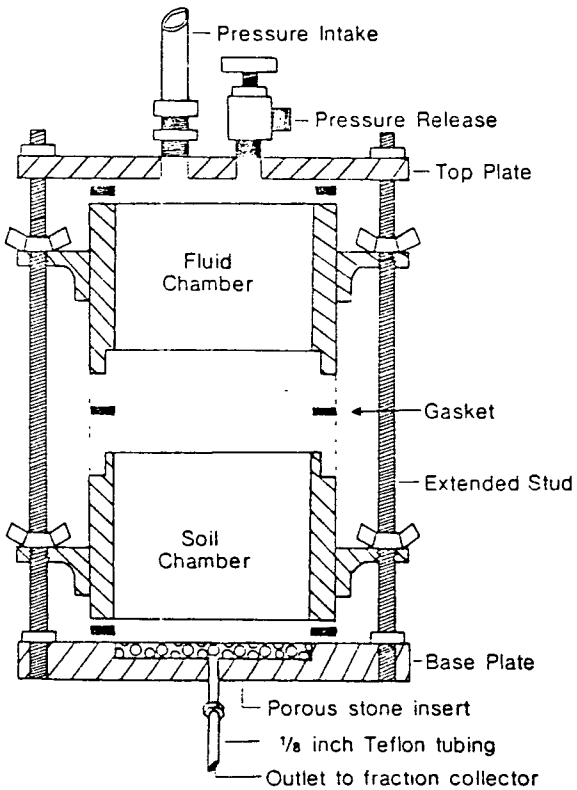


Figure 26 - Schematic of the compaction permeameter.

After preparing a sample in the compaction mold permeameter, the authors pass one pore volume of standard leachate through the clay cores. If the clay has shrunk, they consider it unsuitable as a clay liner, and no further testing is conducted. If it has not changed in volume, they extrude it, weigh it and remount it in the permeameter. Removing the standard leachate is done by passing at least one pore volume of the various leachates through the sample. Again, if the clay core is shrunk, the authors consider it unsuitable for a clay liner. It is the writer's opinion that this test method is inadequate to properly assess the actual effect of organic leachates on clay minerals. Firstly, as mentioned, a backpressure is required to insure saturation. Without such a backpressure, varying degrees of saturation within the clay samples can produce misleading results. Next, it is recommended that these samples be conducted in a triaxial cell, where a consolidation pressure can be applied equivalent to that pressure which the sample will be subsequently subjected to in the field. In this way, an accounting of the in-situ stresses may be made. Further, by testing in a permeameter, the swell potential or the volume changes that the material can experience when alternate pore fluids are introduced cannot be measured. Hence, if the sample shrinks, there could be piping. It is apparent by an examination of Figure 25, that certain of the clay minerals are initially consolidating (shrinking) due to the effect of the fluid and hence there is frequently an initial decrease in permeability. At such a point that the sample pulls away, shrinks or potentially cracks due to this reduction in double layer thickness, an open channel is available for the permeant to penetrate showing extremely large increases in permeability. From the data, the effect of the pore fluid is therefore very difficult to assess. For example, the ethylene glycol treated Houston black core showed a steady decrease in permeability following the initial permeability increase. If the swell and/or shrink volume changes were known, one could better assess the meaning of this change in direction and this change in permeability. An examination of the dielectric constants as

presented on Table 7 shows that, with the exception of the ethylene glycol, all of the materials have a relatively low dielectric constant. All of the permeants have a lower dielectric constant than that of water. Consideration of the Gouy-Chapman theory in the reduction in double layer thickness due to the low dielectric constant would lead to the conclusion that the materials upon introduction to these pore fluids would tend to shrink, and hence a reduction in permeability would be expected. This was generally the case, except that the effects of piping, shrinkage cracks or other leakage due to the testing procedure mask the observable effects.

HAXO (1981)

As part of a study to determine the durability of liner materials for hazardous waste disposal facilities, tests were conducted on bentonite-sand admixes as well as natural clay soils. In a constant head permeability test, wastes including acidic, alkaline, lead and oily wastes were placed above a compacted fine grained soil liner. No determination of soil type, cation exchange capacity, mineral type or other important clay mineralogical parameters is reported. Test results are simply stated in that the fluids collected after more than three years of exposure are essentially neutral and have high solids, mostly salt, content. The mixes of bentonite and sand allowed significant seepage due to channeling along the sidewalls of the testing apparatus. This leaves the writer to further conclude that geotechnical input into the design of testing apparatus for waste compatibility studies is essential.

GREEN, LEE & JONES (1980)

In an effort to evaluate the effects of organic solvents on the shrink/swell

characteristics of clays, a laboratory study of the clay-solvent interaction was undertaken. In these studies, several organic solvents including glycerol, methanol, acetone, trichloroethylene, carbon tetrachloride and xylene were utilized as pore fluids. Three naturally occurring clay soils identified as the Ranger shale, Kosse kaolin and fire clay were utilized. The shrink/swell characteristics were measured in a one-dimensional consolidometer.

The investigators evaluated their data from a physical-chemical and clay mineralogical viewpoint as well as from a macroscopic viewpoint. First, they concluded that the degree of swelling increased as the dielectric constant of the pore fluid increased. A review of the Gouy-Chapman theory indicates that the repulsion forces between particles increase with an increasing dielectric constant. Hence, the increase in the degree of swelling with an increasing dielectric constant is consistent with that behavior predicted from the Gouy-Chapman theory. It was further observed by the investigators that, with some solvents with extremely low dielectric constants such as xylene and carbon tetrachloride, the net volume change was negative (i.e., shrinking). This resulted in cracking within the consolidometer. Again, this is consistent with that predicted from the Gouy-Chapman theory. However, the investigators attributed this phenomenon to soil dehydration, an equally plausible explanation. As the investigators approached this research from a clay mineralogical standpoint, several other findings are presented. It has been found that, as the plasticity index increases, the swelling potential increases (Seed, et al, 1964). This trend was also observed in this study. Review of the clay mineralogy would indicate that the cation exchange capacity should increase with increasing montmorillonitic content. However, this trend was not observed in this study. Also, the montmorillonite content was not found to correlate with the swelling characteristics.

Finally, the investigators concluded that the swelling observed was interparticle swelling, as opposed to intraparticle swelling. This conclusion is based on X-ray diffraction data, which indicated no change in the mineral lattice dimensions that occurred during testing.

GREEN, LEE & JONES (1980)

In a companion study to the one just discussed, the effect of organic solvents on the permeability of clays was studied. The investigators utilized the same clays and pore fluids as just discussed. The permeability tests were conducted on remolded clays in thick walled glass columns. No backpressure was utilized nor were the samples consolidated.

The study found that in general the permeability of clays was consistently lower for organic solvents than with water. It was found that the permeability decreased with time and attained equilibrium in several weeks. The permeability correlated well with the pore fluid dielectric constant; that is, the lower the dielectric constant, the lower the permeability. Finally, it was found that solvents with extremely low dielectric constants could cause clay shrinkage as previously discussed. Such shrinkage resulted in cracking and rapid breakthrough of pore fluids through the clay columns. This caused the transportation of pore fluids in bulk. These data are compatible with those predicted by the Gouy-Chapman theory, as well as the findings of Haxo.

The Gouy-Chapman theory says that, as the dielectric constant goes up, so does the interparticle repulsion, which would make for a more open or disperse structure. Conversely, as the dielectric constant decreases, the structure becomes more flocculated

and tends to shrink. Under these conditions, one would expect the permeability to decrease.

The breakthrough is observed as a result of the experiment design, specifically the testing apparatus. That is, the permeameters could not apply a constant confining stress. As the samples began to shrink, the confining stress decreased. Eventually, this stress was reduced to essentially zero, and leakage between the permeameter wall and the sample was observed.

SUMMARY AND CONCLUSIONS

It is evident that significant work has been done to provide an understanding of the interaction between pore fluids and clay behavior. This research has been conducted in various fields. Geotechnical engineers, in their effort to better understand the fundamentals of clay behavior, have conducted various tests utilizing alternate pore fluids and various clay minerals. Other researchers, looking for a practical application to the liner problems, have studied the effects of organic leachate on various soils used as liners. After reviewing the available data, it is the writer's conclusion that the fundamental concepts of colloid behavior as extracted from the field of colloidal chemistry are applicable to the field of geotechnical engineering. These theories, if better understood by the engineers, can be used as an aid to predict the clay behavior in response to a particular pore fluid. This is only possible if the chemical characterization of the pore fluid is well understood. Hence, with our knowledge of colloidal chemistry, any given test results can often be explained on a microscopic basis utilizing the colloidal chemistry theories.

The findings of various researchers has been reviewed on a case-by-case basis. The results were then examined for compatibility with results predicted from the Gouy-Chapman theory. In most cases the clay behavior due to changes in pore fluid composition were consistent with changes predicted by the Gouy-Chapman theory. The conclusion is drawn that the Gouy-Chapman theory is extremely useful as a predictive tool to study the influence of pore fluid on clay behavior.

To adequately work and understand these phenomena, a characterization of the waste is necessary. In a similar manner to our geotechnical site characterizations, one must understand the general properties of the given waste and how those properties influence the clay behavior from a physical-chemical standpoint. Hence, terms such as polar, nonpolar, aqueous, inaqueous, aqueous organic, aqueous inorganic must not leave the geotechnical engineer bewildered. Finally, it is recognized that considerable additional studies are required in virtually all areas of the effects of hazardous wastes on clays from a physical-chemical standpoint. The phenomena investigated herein are extremely complex and all possible influences could not be addressed in this paper. Studies are required on the very basic levels of understanding clay mineralogy, pore fluid chemistry, and the interaction of a clay mineralogical system with pore fluids. Immediate needs are concerned with adequate and safe methods of conducting permeability tests with hazardous pore fluids on clay materials proposed for liners, which adequately reflect field conditions which these clays will be subjected to while in service. Published data to date indicate that limited consideration has been given to simulating the in-place conditions and the response of clay liners to pore fluids under these conditions.

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